Supporting Information for

A Highly Practical Copper(I)/TEMPO Catalyst System for Chemoselective Aerobic Oxidation of Primary Alcohols

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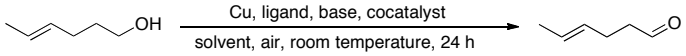
I. General Considerations.

^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer. Chemical shifts (δ) are given in parts per million and referenced to the residual solvent signal;[1] and all coupling constants are reported in Hz. High resolution mass spectra were obtained by the mass spectrometry facility at the University of Wisconsin. GC analyses were performed using a DB-Wax column installed in a Shimadzu GC-17 with FID. Melting points were taken on a Mel-Temp II melting point apparatus. Column chromatography was performed on an Isco Combiflash system using Silicycle 60 silica gel.

All commercial reagents were obtained from Aldrich and used as received unless otherwise noted. CH_3CN was taken from a solvent system which passes the solvent through a column of activated molecular sieves, however no precautions were taken to exclude air or water from the solvent or reaction mixtures and reactions run with undried solvent proceed similarly. Reaction mixtures were monitored by TLC using $KMnO_4$ to visualize plate.

II. General Method for Screening of Catalyst Systems and Reaction Conditions.

Table S1. Optimization of Cu/TEMPO System for the Oxidation of *trans*-4-hexen-1-ol.



	Entry	Cu salt	mol %	Ligand	mol %	cofactor	mol%	base	mol%	Solvent	Conc (M)	Yield[a]
Semmelhack	1	CuCl	10	none		TEMPO	10	none		DMF	0.4	29
	2	CuCl	10	none		TEMPO	10	none		MeCN	0.4	24
	3	Cu(OTf)	10	none		TEMPO	10	none		MeCN	0.4	ND[a]
Marko	4	CuCl	5	Phen	5	DBAD	5	KO*t*Bu NMI	5 7	$PhCF_3$	0.1	36
	5	CuCl	5	Phen	5	DBAD	5	KO*t*Bu NMI	5 7	Tol	0.1	26
	6	CuCl	5	Phen	5	DBAD	5	KO*t*Bu NMI	5 7	$MeCN/H_2O$	0.1	ND[a]
	7	CuCl	5	Phen	5	TEMPO	5	KO*t*Bu NMI	5 7	$MeCN/H_2O$	0.2	12
	8	CuCl	5	Phen	5	TEMPO	5	NMI	7	MeCN	0.2	71
	9	CuCl	5	Phen	5	DBAD	5	NMI	7	MeCN	0.2	8
	10	CuCl	5	bpy	5	TEMPO	5	KO*t*Bu NMI	5 7	$MeCN/H_2O$	0.2	85
	11	CuCl	5	bpy	5	TEMPO	5	KO*t*Bu	5	$MeCN/H_2O$	0.1	11
	12	$CuCl_2$	5	bpy	5	TEMPO	5	KO*t*Bu	5	$MeCN/H_2O$	0.2	14
	13	$CuBr_2$	5	bpy	5	TEMPO	5	KO*t*Bu	5	$MeCN/H_2O$	0.2	23
Sheldon	14	$CuBr_2$	5	bpy	5	TEMPO	5	KO*t*Bu	5	$MeCN/H_2O$	0.67	33
	15	$CuBr_2$	5	bpy	5	TEMPO	5	KO*t*Bu NMI	5 7	$MeCN/H_2O$	0.2	23
	16	$CuBr_2$	5	bpy	5	TEMPO	5	KO*t*Bu	5	MeCN	0.2	100
	17	$CuBr_2$	5	bpy	5	TEMPO	5	KO*t*Bu NMI	5 7	MeCN	0.2	100
	18	$CuBr_2$	5	bpy	5	TEMPO	5	NMI	7	MeCN	0.2	95
	19	CuBr	5	bpy	5	TEMPO	5	NMI	7	MeCN	0.2	98
	20	CuCl	5	bpy	5	TEMPO	5	NMI	7	MeCN	0.2	36
	21	CuCl	5	bpy	5	TEMPO	5	NMI	10	MeCN	0.2	81
	22	CuCl	5	bpy	5	TEMPO	5	KO*t*Bu NMi	5 7	MeCN	0.2	ND[a]
	23	CuCl	5	Phen	5	TEMPO	5	KO*t*Bu NMI	5 7	MeCN	0.2	35
	24	$Cu(BF_4)$	5	bpy	5	TEMPO	5	NMI	10	MeCN	0.2	100
	25	$Cu(PF_6)$	5	bpy	5	TEMPO	5	NMI	10	MeCN	0.2	100
This Work	**26**	**Cu(OTf)**	**5**	**bpy**	**5**	**TEMPO**	**5**	**NMI**	**10**	**MeCN**	**0.2**	**100**
	27	$Cu(OTf)_2$	5	bpy	5	TEMPO	5	NMI	10	MeCN	0.2	ND[a]
	28	Cu(OTf)	5	bpy	5	TEMPO	5	pyridine	10	MeCN	0.2	100
	29	Cu(OTf)	5	bpy	5	TEMPO	5	imidazole	10	meCN	0.2	23
	30	Cu(OTf)	5	bpy	5	TEMPO	5	DBU	10	MeCN	0.2	ND[a]
	31	Cu(OTf)	5	bpy	5	TEMPO	5	2-DMAP	10	MeCN	0.2	88
	32	Cu(OTf)	5	bpy	5	TEMPO	5	DABCO	10	MeCN	0.2	77
	33	Cu(OTf)	5	bpy	5	TEMPO	5	none		MeCN	0.2	92
	34	Cu(OTf)	5	Phen	5	TEMPO	5	NMI	10	MeCN	0.2	100
	35	Cu(OTf)	5	none		TEMPO	5	NMI	10	MeCN	0.2	68
	36	Cu(OTf)	5	bpy	5	none		NMI	10	MeCN	0.2	ND[a]
	37	Cu(OTf)	3	bpy	3	TEMPO	3	NMI	6	MeCN	0.2	99
	38	Cu(OTf)	2	bpy	2	TEMPO	2	NMI	4	MeCN	0.2	76
	39	Cu(OTf)	1	bpy	1	TEMPO	1	NMI	2	MeCN	0.2	35

General Procedure for the screening of Cu/TEMPO reaction conditions (Tables 1 and S1). All reagents were combined in a 13 mm culture tube and the reaction was stirred at room temperature open to air for 24 h. The mixture was then diluted with CH_2Cl_2 (2 mL), filtered through a plug of silica and analyzed by GC. For reactions conducted in MeCN/H_2O, the reaction was diluted with CH_2Cl_2 (3 mL) and H_2O (3 mL), the layers separated, and the aqueous layer washed once with CH_2Cl_2 (3 mL). The combined organics were analyzed by GC. Yields are given as P/(P+SM) not accounting for response factors.

General method for oxidation of functionalized alcohols and unprotected diols with $Pd(OAc)_2$/py (Tables 2 and 5). Reactions were carried out according to the literature procedure.[2] To $Pd(OAc)_2$ (2.25 mg, 0.01 mmol) and 3Å molecular sieves (100 mg) in a 13 mm culture tube was added a solution of pyridine (3.2 μL, 0.04 mmol) in toluene (1.2 mL). The tube was fitted with a septum and an O_2 balloon and heated at 80 °C for 10 min, before a solution of the alcohol (0.20 mmol) in toluene (0.8 mL) was added by syringe. The mixture was allowed to react for 2 h, before it was cooled to room temperature, filtered through celite, diluted with EtOAc, and analyzed by GC.

General method for oxidation of functionalized alcohols and unprotected diols with $RuCl_2(PPh_3)_3$/TEMPO (Tables 2 and 5). Reactions were carried out according to the literature procedure[3] The appropriate alcohol (0.50 mmol), $RuCl_2(PPh_3)_3$ (9.6 mg, 0.01 mmol), and TEMPO (4.7 mg, 0.06 mmol) were combined with 1.0 mL toluene in a 13 mm cultre tube fitted with a septum and an O_2 balloon. The reaction mixture was heated at 100 °C for 7h, after which time the reaction mixture was cooled to room temperature, filtered through celite, diltured with EtOAC, and analyzed by GC.

General method for the oxidation of functionalized alcohols and unprotected diols with (bpy)Cu/TEMPO/KO*t*Bu (Tables 2 and 5). Reactions were carried out with only slight modification of the literature procedure.[4] To a solution of alcohol (0.25 mmol) in a mixture of CH_3CN (0.4 mL) and H_2O (0.25 mL) was added sequentially (1) a solution of KO*t*Bu in H_2O (0.25 mL, 50 mM), (2) a solution of $CuBr_2$ in CH_3CN (0.20 mL, 60 mM), (3) a solution of bpy in CH_3CN (0.20 mL, 60 mM), (4) a solution of TEMPO in CH_3CN (0.20 mL, 60 mM). The reaction mixture was stirred open to air for 24 h. The mixture was then diluted with CH_2Cl_2 (3 mL) and H_2O (3 mL), the layers separated, and the aqueous layer extracted once more with CH_2Cl_2 (3 mL). The combined organics were analyzed by GC.

General method for the oxidation of functionalized alcohols and unprotected diols with (bpy)Cu/TEMPO/NMI (Tables 2 and 5). To a solution of alcohol (0.25 mmol) in CH_3CN (0.25 mL) in a 13 mm culture tube was added sequentially a solution of (1) CuOTf (0.25 mL, 0.05M), (2) bpy (0.25 mL, 0.05M), (3) TEMPO (0.25 mL, 0.05M), and (4) NMI (0.25 mL, 0.10M). The reaction mixture was stirred at room temperature open to air for 24 h. The mixture was then diluted with CH_2Cl_2 (3 mL), filtered through a plug of silica and analyzed by GC.

III. Methods for Gas Uptake Kinetic Analyses on Cu/TEMPO Systems.

Comparison of Cu/TEMPO Systems in the oxidation of 1-octanol (reactions shown in Figure 1). For each reaction, the Cu catalyst (below) was added to a 50 mL roundbottom flask with stirbar. The flasks were attached to an apparatus with a calibrated volume and a pressure transducer designed to measure the gas pressure within each of 5 sealed reaction vessels. The apparatus was evacuated and filled with O_2 to 900 torr three times. The pressure was established at 700 torr and the flasks heated to 27 °C. Solution A (below) was added via syringe through a septum, and the pressure and temperature allowed to equilibrate. When the pressure and temperature stabilized, Solution B was added via syringe through a septum. Data were acquired using custom software written within LabVIEW (National Instruments).

Reaction	Cu Catalyst	Solution A	Solution B
1 Semmelhack	CuCl (9 mg, 0.10 mmol)	2.0 mL DMF	1-octanol (130 uL, 1 mmol) TEMPO (16 mg, 0.10 mmol) In 0.5 mL DMF
2 Sheldon	$CuBr_2$ (11 mg, 0.05 mmol) bpy (8 mg, 0.05 mmol)	0.5 mL MeCN	1-octanol (130 uL, 1 mmol) TEMPO (8 mg, 0.05 mmol) In 0.5 mL MeCN KO*t*Bu (5.6 mg, 0.05 mmol) In 0.5 mL H2O
3 This work	Added as solution B since all components are soluble	1-octanol (130 uL, 1 mmol) in 4 mL MeCN	Cu(OTf) (17.5 mg, 0.5 mmol) bpy (8 mg, 0.05 mmol) TEMPO (8 mg, 0.05 mmol) NMI (8 μL, 0.05 mmol) In 1 mL MeCN

For Cu Salt Dependence (reactions shown in Figures 2 and S1). For each reaction, 0.025 mmol of the Cu catalyst (below) was added to a 50 mL roundbottom flask with stirbar. The flasks were attached to an apparatus with a calibrated volume and a pressure transducer designed to measure the gas pressure within each of 5 sealed reaction vessels. The apparatus was evacuated and filled with O_2 to 900 torr three times. The pressure was established at 500 torr and the flasks heated to 27 °C. 1.5 mL of MeCN was added to each flask via syringe through a septum, and the pressure and temperature allowed to equilibrate. When the pressure and temperature stabilized, the remaining reaction components were added as two solutions: (1) 0.5 mL of TEMPO (0.05 M), bpy (0.05 M) and NMI (0.1M) in MeCN and (2) 0.5 mL of alcohol (1 M) in MeCN were added via syringe through a septum. Data were acquired using custom software written within LabVIEW (National Instruments).

Reaction	Cu Catalyst
1	$CuBr_2$
2	$Cu(OTf)_2$
3	CuBr
4	Cu(OTf)

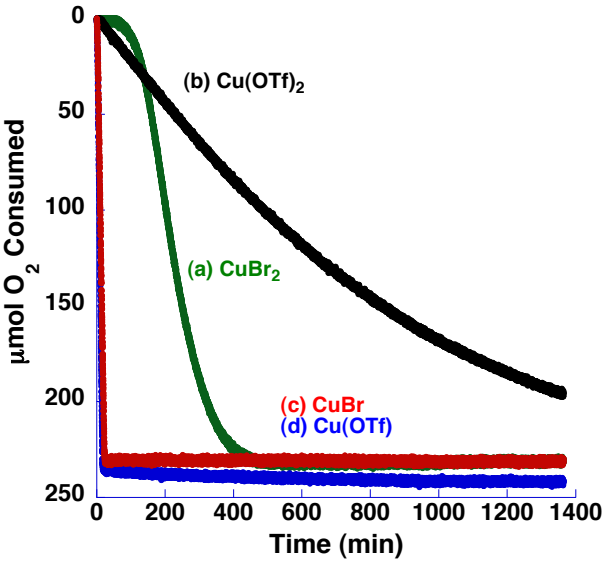


Figure S1. Effect of Cu source on the rate of aerobic oxidation of benzyl alcohol (0.5 mmol) at 27 °C. The Cu source (5 mol %) was combined with TEMPO (5 mol %), NMI (10 mol %), and bpy (5 mol %) with [Cu] = (a) $CuBr_2$ (● , green), (b) $Cu(OTf)_2$ (● , black), and (c) CuBr (● , red), and (d) Cu(OTf) (● , blue). Reactions employing $CuBr_2$ consistently exhibit a long induction period.

IV. The Selective Oxidation of Primary Alcohols.

All alcohols were obtained from commercial sources and used as received, except furyl alcohol which was distilled prior to use. Aldehyde products were isolated and the ^{1}H and ^{13}C NMR spectra compared to literature values. For those not readily available in the literature, full characterization is provided below.

Representative Procedure for the Oxidation of Simple and Functionalized Alcohols. To a solution of alcohol (1 mmol) in dry CH_3CN, (1 mL) in a 20 mm culture tube were added the following solutions: (1) $[Cu(MeCN)_4]X$ (X = OTf^-, BF_4^-, or PF_6^-, 0.05 mmol in 1 mL CH_3CN) (2) 2,2'-dipyridyl (0.05 mmol in 1 mL CH_3CN) (3) TEMPO (0.05 mmol in 1 mL CH_3CN) (4) *N*-methyl imidazole (0.1 mmol in 1 mL CH_3CN). The dark red/brown reaction mixture was stirred rapidly open to air and monitored by TLC until no starting material remained (often accompanied by a change in reaction color to blue/green). Preliminary studies indicate that the reactions described here are not subject to mass transfer effects, and rate of mixing and stir bar shape does not have a significant impact on the outcome of the reaction.

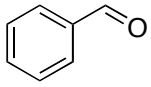
Larger scale reactions were run in the appropriately sized round bottom flask:
10 mmol scale reactions were carried out with 50 mL of CH_3CN in a 250 mL flask.
50 mmol scale reactions were carried out with 250 mL of CH_3CN in a 1 L flask.
Reactions to form volatile aldehydes were carried out in a roudbottom flask fitted with a reflux condenser, a septum, and a balloon of house air or O_2.

Purification Method A.
Upon completion by TLC, the reaction mixture was diluted with 1:1 ether:pentane (20 mL) and filtered through a plug of silica with rinsing. The solvent was evaporated to yield the aldehyde which was pure by ^{1}H and ^{13}C NMR spectroscopies. Residual TEMPO was evident by GC analysis, and can be removed with silica column chromatography (as in Purification Method B)

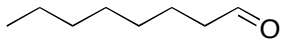
Purification Method B.
Upon completion by TLC, the solvent was removed and the crude reaction mixture purified by silica column chromatography.

Purification Method C, for volatile aldehydes.
For a 1 mmol scale reaction:
Upon completion by TLC, the reaction mixture was quenched by the addition of water (25 mL) and pentanes (25 mL). The layers were separated and the aqueous layer was extracted with pentanes (2 x 25 mL), washed with brine (25 mL) and dried over Na_2SO_4. Evaporation of the solvent at 0 °C gave the title compound as a lightly colored liquid or oil.

V. Characterization of Aldehyde Products.



Benzaldehyde. Using $[Cu(MeCN)_4](PF_6)$. The reaction was run in a 20 mm culture tube open to air. Upon completion by TLC (3 h, R_f(aldehyde) = 0.82 and R_f(alcohol) = 0.62 in 2:1 Hex:EtOAc), the reaction mixture was diluted with EtOAc and filtered through a silica plug to yield 99.8 mg (0.94 mmol, 95 % y) of the title compound as an oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.06 (s, 1 H, C(O)*H*), 7.92 (d, *J* = 7, 2H, *ortho*), 7.67 (t, J = 7, 1 H, *para*), 7.57 (t, *J* = 7.5, 2H, *meta*). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 191.43 (*C*HO), 135.44, 133.52, 128.78, 128.07. Spectral properties are consistent with literature values.[5]

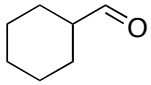


Octanal. In each case below, the reaction was run in a 20 mm culture tube open to air. Upon completion by TLC (R_f(aldehyde) = 0.94 and R_f(alcohol) = 0.71 in 2:1 Hex:EtOAc), the product was purified by Purification Method C to yield a lightly colored oil.

Using $[Cu(MeCN)_4](BF_4)$: 23 h, 137 mg, 1.07 mmol, 98% y.

Using $[Cu(MeCN)_4](OTf)$: 22 h, 132 mg, 1.03 mmol, >98% y.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.77 (t, *J* = 1.8, 1 H, C*H*O), 2.43 (dt, *J* = 7.5, 1.8, 2H, CH_2CHO), 1.64 (m, 2H, CH_2), 1.31 (m, 8H, 4CH_2), 0.89 (t, *J* = 7.2, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 202.88 (*C*HO), 43.87, 31.56, 29.07, 28.95, 22.53, 22.04, 13.99. Spectral properties are consistent with literature values.[6]

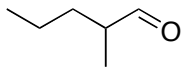


Cyclohexanecarbaldehyde. In each case below, the reaction was run in a 20 mm culture tube fitted with a septum and a balloon. Upon completion by TLC (R_f(aldehyde) = 0.97, R_f(alcohol) = 0.62, in 2:1 Hex:EtOAc), the product was purified by Purification Method C to yield the title compound as a lightly colored oil.

Using a balloon of house air and $[Cu(MeCN)_4](OTf)$: 24 h, 102 mg, 0.91 mmol, 92% y.

Using a balloon of O_2 and $[Cu(MeCN)_4](BF_4)$: 11 h, 99.8mg, 0.98 mmol, 88% y.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.63 (s, 1 H, C*H*O), 2.25 (m, 1 H, C*H*), 1.91 (m, 2H, CH_2), 1.77 (m, 2H, CH_2), 1.66 (m, 1 H, CH_2), 1.4-1.2 (m, 5H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 204.80 (*C*HO), 49.70, 25.75, 25.70, 24.80. Spectral properties are consistent with literature values.[7]

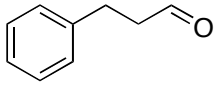


2-methyl pentanal. In each case below, the reaction was run in a 20 mm culture tube fitted with a septum and a balloon. Upon completion by TLC (R_f(aldehyde) = 0.97, R_f(alcohol) = 0.67, in 2:1 Hex:EtOAc), the product was purified by Purification Method C to yield the title compound as a lightly colored oil.

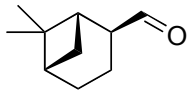
Using a balloon of house air and $[Cu(MeCN)_4](OTf)$: 24 h, 85 mg, 0.85 mmol, 83% y.

Using a balloon of O_2 and $[Cu(MeCN)_4](BF_4)$: 11 h, 100. mg, 1.00 mmol, 98% y.

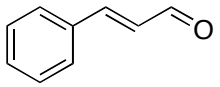
^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.64 (d, *J* = 2.1, 1 H, C(O)*H*), 2.37 (m, 1 H, C*H*), 1.71 (m, 1 H, CH_2), 1.39 (m, 3H, CH_2), 1.11 (d, *J* = 7.2, 3H, CH_3), 0.95 (t, *J* = 7, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 205.22 (*C*O), 45.92, 32.47, 19.94, 13.89, 13.12. Spectral properties are consistent with literature values.[8]



3-phenyl propanal.
Purification Method A: Using $[Cu(MeCN)_4](PF_6)$. The reaction was run in a 20 mm culture tube open to air. Upon completion by TLC (5.5h, R_f(aldehyde) = 0.77 and R_f(alcohol) = 0.42 in 2:1 Hex:EtOAc), the reaction mixture was diluted with 1:1 pentanes/ether and filtered through a silica plug, to yield 131 mg (0.97 mmol, >98% y) of the title compound as an oil.
Purification Method B: Using $[Cu(MeCN)_4](OTf)$. The reaction was run in a 250 mL roundbottom and reached completion in 3.5 h. Chromatographic purification (gradient elution of EtOAc in Hex,) yielded 1.30 g (9.69 mmol, 97 % y) of a slightly colored oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.87 (t, *J* = 1.5, 1 H, C*H*O), 7.38-7.21 (m, 5H, Ph), 3.01 (t, *J* = 7.5, 2 H, CH_2), 2.84 (t, *J* = 7.5, 2 H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 201.52 (*C*O), 140.33, 128.61, 128.29, 126.30, 45.29, 28.14. Spectral properties are consistent with literature values.[9]

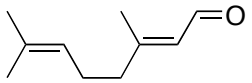


(1S, 2S, 5S)-(-)-myrtanal. Using $[Cu(MeCN)_4](OTf)$. The reaction was run in a 20 mm culture tube open to air. Upon completion by TLC (24 h, R_f(aldehyde) = 0.88 and R_f(alcohol) = 0.64 in 10% EtOAc in Hex), the reaction mixture was diluted with EtOAc and filtered through a silica plug to yield 149 mg (0.98 mmol, 99% y) of the title compound as an oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.63 (s, 1 H, C*H*O), 2.81 (t, *J* = 8.4, 1 H, C*H*), 2.28 (t, *J* = 1.6, 1 H), 2.14 (m, 2 H), 1.90 (m, 3 H), 1.62 (m, 1 H), 1.29 (buried m, 1 H), 1.29 (s, 3 H, CH_3), 0.92 (s, 3 H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 203.52 (*C*O), 48.53, 39.97, 39.71, 38.90, 25.72, 23.39, 23.02, 19.92, 12.34. Spectral properties are consistent with literature values and indicate no epimerization to form the (1S, 2R, 5S)-(-)-myrtanal product.[10]



Cinnamaldehyde. Using $[Cu(MeCN)_4](OTf)$. The reaction was run in a 20 mm culture tube open to air. Upon completion by TLC (2 h, R_f(aldehyde) = 0.70 and R_f(alcohol) = 0.42 in 2:1 Hex:EtOAc), the reaction mixture was concentrated and purified by silica column chromatography (Purification Method B, gradient elution of EtOAc in Hex) to yield 130 mg (0.98 mmol, 92 % y) of the title compound as an oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.72 (d, *J* = 7.8, 1 H, C*H*O), 7.59 (m, 2 H, Ar and C=C*H*), 7.44 (m, 4H, Ar), 6.74 (dd, *J* = 16, 7.8, 1H, C=C*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.69, 152.77, 134.04,

131.29, 129.12, 128.66, 128.51. Spectral properties are in agreement with a commercially obtained sample.



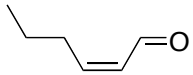
Geranial. In each case below, the reaction was run in a 20 mm culture tube open to air. Upon completion by TLC (R_f(aldehyde) = 0.94 and R_f(alcohol) = 0.76 in 1:1 Hex:EtOAc), the product was purified by Purification Method C to yield a lightly colored oil.

Using $[Cu(MeCN)_4](PF_6)$: 163mg, 1.07 mmol, >99% y.

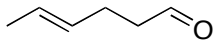
Using $[Cu(MeCN)_4](BF_4)$: 149 mg, 0.98 mmol, 97% y.

Using $[Cu(MeCN)_4](OTf)$: 156 mg, 1.02 mmol, >98% y.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.0 (d, *J* = 8, 1 H C(O)*H*), 5.89 (d, *J* = 8, 1 H, C=C*H*), 5.07 (m, 1 H, C=C*H*), 2.23 (m, 4H, 2CH_2), 2.17 (s, 3H, CH_3), 1.69 (s, 3H, CH_3), 1.61 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 191.51 (*C*OH), 164.01, 133.15, 127.65, 122.78, 40.84, 25.97, 25.87, 17.94, 17.81. Spectral properties are consistent with literature values.[5]



***Cis*-hexenal.** Using $[Cu(MeCN)_4](OTf)$. The reaction was run in a 20 mm culture tube open to air and monitored by GC. Upon completion, the reaction mixture was purified by aqueous extraction with pentanes (Purificaiton Method C), to yield 96 mg (0.97 mmol, <98% y) of the title compound as a light pink oil (20:1 *cis*:*trans* by ^{1}H NMR spectroscopy). Reactions that are not stopped after completion result in isomerization of of the alkene. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.11 (d, *J* = 8, 1 H, C*H*O), 6.65 (m, 1H, =C*H*), 5.99 (m, 1 H, =C*H*), 2.61 (dt, *J* = 8, 1.5, 2 H, CH_2), 1.57 (m, 2 H, CH_2), 0.99 (t, *J* = 7.5 3 H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 188.95 (*C*HO), 151.19 (=*C*H), 128.42 (=*C*H), 27.90, 20.44, 11.60. Spectral properties are consistent with literature values.[11]



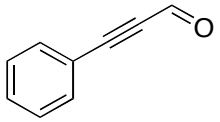
***Trans*-4-hexenal.** In each case below, the reaction was run in a 250 mL roundbottom flask with a water condenser. Upon completion by TLC (R_f(aldehyde) = 0.82 and R_f(alcohol) = 0.58 in 2:1 Hex:EtOAc), the product was purified by Purification Method C to yield a lightly colored oil.

Using a condenser open to ambient air, $[Cu(MeCN)_4](PF_6)$:
24 h, 0.70 g, 7.1 mmol, 69% y.

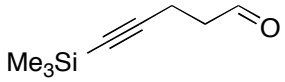
Using a condenser fitted with a septum and a balloon of house air, $[Cu(MeCN)_4](OTf)$:
24 h, 0.96 g, 9.8 mmol, 88% y.

Using a condenser fitted with a septum and a balloon of O_2 and $[Cu(MeCN)_4](OTf)$:
6.5 h, 0.89g, 9.1 mmol, 92% y.

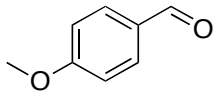
^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.69 (t, *J* = 1.5, 1 H, C*H*O), 5.39 (m, 2 H, 2 =C*H*), 2.42 (dt, *J* = 7, 1.5, 2 H, CH_2CHO), 2.25 (quart, *J* = 6.5, 2 H, =CH_2CH_2), 1.58 (d, *J* = 4.5, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 202.35 (*C*HO), 128.84, 126.33, 43.43, 25.09, 17.79. Spectral properties are consistent with literature values.[12]



3-Phenyl-2-propynal. Using $[Cu(MeCN)_4](PF_6)$. The reaction was run in a 20 mm culture tube open to air. Upon completion by TLC (2 h, R_f(aldehyde) = 0.86 and R_f(alcohol) = 0.59 in 2:1 Hex:EtOAc), the reaction mixture was purified by Purification Method A to yield 137 mg (1.05 mmol, >98% y) of the title compound as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.44 (s, 1 H, C*H*O), 7.62 (d, *J* = 7.2, 2 H, *o*Ar), 7.49 (t, *J* = 6.6, 1 H, *p*Ar), 7.42 (t, *J* = 6.6, 2 H, *m*Ar). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 177.00 (*C*HO), 133.51, 131.53, 128.97, 119.68, 95.35 (*C*≡C), 88.67 (*C*≡C). Spectral properties are consistent with literature values.[13]



5-trimethylsilyl-4-pentynal. Using $[Cu(MeCN)_4](PF_6)$. The reaction was run in a 20 mm culture tube open to air for 24 h, and did not reach completion by TLC (R_f (aldehyde) = 0.86, R_f(alcohol) = 0.46, in 2:1 Hex:EtOAc). The reaction mixture was purified by aqueous workup (Purification Method C) to afford the title compound in 86%y (135 mg, 0.87 mmol) in >95% purity by ^{1}H NMR spectroscopy. The product mixture was further purified by silica column chromatograpy (EtOAc in Hex gradient elution) to yield 102 mg (0.66 mmol, 65% y) of the title compound as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.79 (t, *J* = 1.2, 1 H, C*H*O), 2.67 (m, 2 H, CH_2), 2.54 (m, 2 H, CH_2), 0.13 (s, 9 H, Si(CH_3)$_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 200.34, 104.71, 85.79, 42.53, 13.12, 0.01. Spectral properties are consistent with literature values.[14]

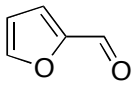


4-methoxy benzaldehyde.

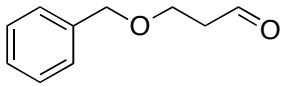
Purification Method A: Using $[Cu(MeCN)_4](OTf)$. The reaction was run in a 20 mm culture tube open to air. Upon completion by TLC (2.5 h, R_f(aldehyde) = 0.70 and R_f(alcohol) = 0.41 in 2:1 Hex:EtOAc), the reaction mixture was diluted with 1:1 pentanes/ether and filtered through a silica plug, to yield 136 mg (0.995 mmol, >98% y) of the title compound as a lightly colored oil.

Purification Method B: Using $[Cu(MeCN)_4](OTf)$: The reaction was run in a 1 L roundbottom and reached completion in 1.5 h. Chromatographic purification (gradient elution of EtOAc in Hex,) yielded 6.72 g (49.3 mmol, 96 % y) of a colorless oil.

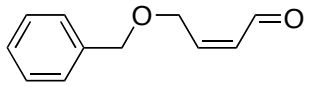
^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.91 (s, 1 H, C*H*O), 7.86 (d, *J* = 9, 2 H, Ar), 7.02 (d, *J* = 9, 2 H, Ar), 3.91 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 190.91 (*C*HO), 164.72 (Ar *ipso*), 132.54 (Ar), 130.12 (Ar), 114.44 (Ar), 55.71 (O*C*H_3). Spectral properties are consistent with literature values.[5]



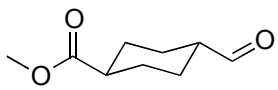
Furfural. Using $[Cu(MeCN)_4](PF_6)$. The reaction was run in a 20 mm culture tube fitted with an air balloon. Upon completion by TLC (3 h, R_f = 0.79, alcohol R_f = 0.65, in 2:1 Hex:EtOAc), the reaction mixture was purified by aqueous workup (Purification Method C) to yield 81.2 mg (8.5 mmol, 83% y) of the title compound as a lightly colored oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.68 (s, 1 H, C*H*O), 7.70 (m, 1 H), 726 (d, *J* = 3.6, 1 H), 6.61 (dd, *J* = 3.6, 1.8, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 177.03 (*C*HO), 152.11, 147.32, 120.14, 111.76. Spectral properties are consistent with literature values.[5]



3-benzyloxy-propionaldehyde. Using $[Cu(MeCN)_4](BF_4)$. The reaction was run in a 20 mm culture tube open to air. Upon completion by TLC (5 h, R_f(aldehyde) = 0.68 and R_f(alcohol) = 0.32 in 2:1 Hex:EtOAc), the reaction mixture was diluted with 1:1 pentanes/ether and filtered through a silica plug, to yield 184.1 mg (1.12 mmol, >98% y) of the title compound as a lightly colored oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.79 (t, *J* = 1.8, 1 H, C*H*O), 7.33 (m, 5 H, Ar), 4.53 (s, 2 H, CH_2), 3.81 (t, *J* = 6, 2 H, CH_2), 2.69 (td, *J* = 6, 1.8, 2 H, CH_2).). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 201.17, 137.95, 128.51, 127.83, 127.76, 73.30, 63.92, 43.92. Spectral properties are consistent with literature values.[15]

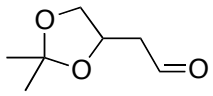


(Z)-4-benzyloxy-but-2-enal. Using $[Cu(MeCN)_4](BF_4)$. The reaction was run in a 20 mm culture tube open to air and the reaction monitored by colored and quenched when the reaction mixture changed from dark red to green. Upon completion (1.5 h) the reaction mixture was diluted with EtOAc and passed through a silica plug to yield 181 mg (1.03 mmol, >98% y) of the title compound as a pink oil (19:1 *cis*:*trans* by ^{1}H NMR spectroscopy). Reactions of (Z)-4-benzyloxy-but-2-en-1-ol that are not stopped immediately after completion result in increased amounts of the *trans* isomer. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.06 (d, *J* = 6.6, 1 H, C*H*O), 7.3 (m, 5H, Ph), 6.644 (dt, *J* = 10.8, 5.4, 1H, =C*H*), 6.06 (m, 1H, =C*H*), 4.60 (s, 2 H, CH_2Ph), 4.53 (dd, *J* = 5.7, 1.8). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 191.43 (*C*HO), 137.37, 129.74, 128.57, 128.02, 127.82, 73.08, 66.98. Spectral properties are consistent with literature values.[16]

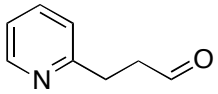


***trans*-formylcyclohexane carboxylic acid methyl ester.** Using $[Cu(MeCN)_4](OTf)$. The reaction was run in a 20 mm culture tube open to air in a 50 °C oil bath. After 24 h the reaction mixtures was diluted with EtOAC and filtered through a silica plug, to yield 179 mg (1.05 mmol, >98% y) of the title compound as a lightly colored oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.63 (d, *J* = 1, 1 H, C*H*O), 3.68 (s, 3 H, CH_3), 2.26 (m, 2 H), 2.09 (m, 4 H), 1.51 (m, 2 H), 1.33 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 204.05 (*C*O), 175.94 (*C*O_2Me), 51.89, 49.57, 42.74, 27.91, 25.27. HPLC analysis (Thermo Scientific

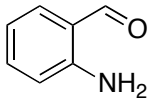
HyperCarb, 100 mm x 4.6 mm x 5 micron, Mobile Phase C 0.1 M $KHSO_4$ in H_2O, Mobile Phase D CH_3CN, 1.0 mL/min; 0 min 95% C 5 % D, 15 min 50% D 50% D, 30.1 min 95% C 5% D, 35 min run, detection at 210 nm, *cis* eludes at 10.0 min, *trans* eludes at 11.75 min) shows *trans*:*cis* >98:2.[17]



(2,2-dimethyl-[1,3]dioxolan-4-yl)-acetaldehyde. Using $[Cu(MeCN)_4](OTf)$. The reaction was run in a 20 mm culture tube fitted with an O_2 balloon at room temperature. After 24 h, the reaction mixture was purified by aqueous extraction (Purification Method C) to yield a mixture of the title compound (78 % y by ^1H NMR spectroscopy) and starting alcohol. The crude reaction product was purified by silica column chromatography to yield 70.5 mg (0.49 mmol, 47%y) of the title compound as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 9.75 (t, *J* = 1.5, 2 H, C*H*O), 4.482 (quint, *J* = 6.6, 1 H), 4.14 (dd, *J* = 8, 6, 1 H), 3.54 (dd, *J* = 8, 6.6, 1 H), 2.79 (ddd, *J* = 17.1, 6, 1.8, 1 H, CH_2), 2.59 (ddd, *J* = 17.1, 6, 1.2, 1 H, CH_2), 1.37 (s, 3 H, CH_3), 1.31 (s, 3 H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): 200.06 (*C*O), 109.38, 70.79, 69.26, 47.98, 26.92, 25.57. Spectral properties are consistent with literature values.[18]



3-pyridine-propionaldehyde. Using $[Cu(MeCN)_4](OTf)$. The reaction was run in a 20 mm culture tube open to air. Upon completion as determined from monitoring by GC, the crude reaction mixture was loaded directly onto silica gel and purified by flash chromatography (100% EtOAC) to yield 130. mg (0.962 mmol, 95% y) of the title compound as a colorless oil. Allowing the reaction to continue after completion resulted in decomposition of the aldehyde in the reaction mixture and reduced yields. ^1H NMR (300 MHz, $CDCl_3$): δ = 9.85 (t, *J* = 1.2, C*H*O), 8.48 (d, *J* = 5.1, 1 H, Ar), 7.56 (td, *J* = 7.5, 1.8, 1 H, Ar), 7.16 (d, *J* = 7.8, 1 H, Ar), 7.08 (m, 1 H, Ar), 3.11 (t, *J* = 6.9, 2 H, CH_2), 2.91 (t, *J* = 7.5, 2 H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 201.42 (*C*HO), 159.76, 149.25, 136.49, 123.09, 121.42, 42.66, 30.35. Spectral properties are consistent with literature values.[19]



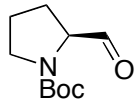
2-amino benzaldehyde. In each case below, the reaction was run in a 20 mm culture tube open to air. Upon completion by TLC (R_f(aldehyde) = 0.91 and R_f(alcohol) = 0.35 in 1:1 Hex:EtOAc), the product was purified by Purification Method A to yield a lightly colored oil.

Using $[Cu(MeCN)_4](BF_4)$: 4 h, 123.4 mg, 1.02 mmol, >98% y.

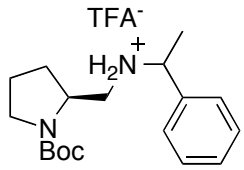
Using $[Cu(MeCN)_4](OTf)$: 3 h, 127.8 mg, 1.05 mmol, >98% y.

^1H NMR (300 MHz, $CDCl_3$): δ = 9.89 (s, 1 H, C(O)*H*), 7.50 (d, *J* = 7.5, 1 H), 7.33 (t, *J* = 7.5, 1 H), 6.77 (t, *J* = 7.5, 1 H), 6.66 (d, *J* = 8, 1 H), 6.12 (br s, 2 H, NH_2). ^{13}C NMR (75

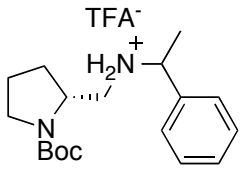
MHz, $CDCl_3$): δ = 194.03 (*C*HO), 149.84, 135.69, 135.16, 118.86, 116.37, 116.01. Spectral properties are consistent with literature values.[20]



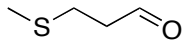
***N*-Boc-L-prolinal.** Using $[Cu(MeCN)_4](PF_6)$. The reaction was run in a 20 mm culture tube open to air at 70 °C. Upon completion by TLC (21 h, R_f(aldehyde) = 0.55 and R_f(alcohol) = 0.24 in 2:1 Hex:EtOAc), the reaction mixture was diluted with 1:1 ether:pentanes and filtered through a silica plug (Purification Method A). Evaporation of the solvent afforded 205 mg (1.03 mmol, >98% y) of the title compound as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, mixture of rotamers): δ = 9.56 (s, 1 H, C*H*O, minor), 9.46 (d, *J* = 3, 1 H, C*H*O, major). 4.20 (m, 1 H, C*H*, minor), 4.05 (m, 1 H, C*H*, major), 3.51 (m, 5 H, major and minor) 2.08 (m, 2 H). 1.99-1.84 (m, 3 H), 1.48 (s, 9H, C(CH_3)$_3$, minor), 1.42 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (75 MHz, $CDCl_3$, mixture of rotamers): δ = 200.73 (minor), 200.50 (major), 155.10 (minor), 154.06 (major), 80.73 (major), 80.31 (minor), 65.12 (major), 65.97 (minor), 46.95 (minor), 46.83 (major), 28.48 (minor), 28.37 (major), 28.09 (major), 26.82 (minor), 24.73 (minor), 24.06 (major). Spectral properties are consistent with literature values.[21]



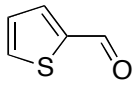
2-[(R-1-[phenyl-ethylammoinum)-methyl]-*N*-Boc-L-pyrrolidine trifluoroacetate. The title compound was made by modification of literature procedure.[22] To a solution of *N*-Boc-L-Prolinal (49.4 mg, 0.25 mmol) in dichloromethane (10mL) was added (R)-(+)-α-methyl benzyl amine (35 μ, 0.275 mmol). The reaction mixture was cooled to 0 °C and catalytic acetic acid (10 μL, 0.15 mmol) was added and the mixture stirred for 10 min before the addition of $NaBH(OAc)_3$ (65.8 mg, 0.30 mmol). The reaction was allowed to stir at room temperature and monitored by TLC. After 1 h, the reaction was dilulted with dichloromethane (20 mL), and quenched with the dropwise addition of a saturated NH_4Cl solution. The layers were separated and the organic layer washed with 5% HCl, 5% $NaHCO_3$, and brine, dried over Na_2SO_4 and filtered. To the filtrate was added 1 mL trifluoroacetic acid, the mixture allowed to stir at room temperature for 5 min, before evaporation of the volatiles to yield 95.4 mg, (0.23 mmol, 91 % yield) of the title compound as a lightly colored oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ =10.0 (br s, 1 H, N*H*), 9.84 (br s, 1 H, N*H*), 7.40 (m, 5 H, Ph), 4.27 (m, 1 H, NH_2C*H*), 3.97 (quart, *J* = 8, 1 H), 3.43 (m, 1 H), 3.27 (m, 1 H), 3.12 (m, 1 H), 2.53 (quart, *J* = 10, NBocC*H*), 2.17 (m, 1 H), 2.17 (dq, *J* = 8, 5, 1 H), 1.71 (d, *J* =6, 3 H, CH_3), 1.47 (s, 9 H, CCH_3). No epimerization was observed by ^{1}H NMR spectroscopy. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.73 (*C*O), 135.80 (Ar), 129.77 (Ar), 129.59 (Ar), 127.48 (Ar), 82.11 (*C*CH_3), 58.64, 55.52, 51.33, 48.05, 31.16, 28.41, 23.72, 20.77. HRMS (EI) [M^+]/z.



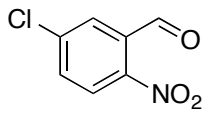
2-[(R-1-[phenyl-ethylammoinum)-methyl]-*N*-Boc-D-pyrrolidine trifluoroacetate. The title compound was made according to the procedure given above using *N*-Boc-D-Prolinal and was isolated as a lightly colored oil in 89% yield (95.4 mg, 0.23 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.15 (br s, 1 H, N*H*), 9.68 (br s, 1 H, N*H*), 7.42 (m, 5 H, Ph), 4.31 (br quart, 1 H, NH_2C*H*), 3.89 (quart, *J* = 8.4, 1 H), 3.44 (m, 1 H), 3.25 (m, 1 H), 3.17 (m, 1 H), 2.80 (br quart, NBocC*H*), 2.08 (m, 1 H), 1.78 (m, 2 H), 1.70 (d, *J* =6, 3 H, CH_3), 1.47 (s, 9 H, CCH_3). No epimerization was observed by ^{1}H NMR spectroscopy.^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.14 (*C*O), 135.49 (Ar), 129.82 (Ar), 129.58 (Ar), 127.60 (Ar), 82.35 (*C*CH_3), 58.71, 55.66, 50.96, 47.99, 30.67, 28.38, 23.69, 18.96. HRMS (EI) [M^+]/z.



3-methylsulfanyl-propionaldehdye. Using [$Cu(MeCN)_4$](OTf). The reaction was run in a 20 mm culture tube open to air at room temperature. Upon completion, the reaction mixture was diluted with 1:1 ether/pentanes and filtered through a silica plug to yield 96.4 mg (0.92 mmol, 96% y) of the title compound as an oil in 94% purity as determined by ^{1}H NMR spectroscopy. The product mixture was further purified by silica column chromatography to yield 25.3 mg (0.24 mmol, 25% y) of the title compound as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.77 (t, *J* = 1.2, 1 H, C*H*O), 2.75 (m, 4 H, 2 CH_2), 2.11 (s, 3 H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 200.78 (*C*HO), 43.43, 26.63, 15.78. HRMS (EI) [M^+]/z calcd. 104.0291, found 104.0284.

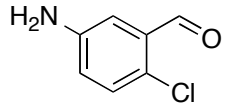


2-thiophenecarboxdaldehyde. Using [$Cu(MeCN)_4$](PF_6). The reaction was run in a 20 mm culture tube open to air. upon completion by TLC (3 h, R_f(aldehyde = 0.91 and R_f(alcohol) = 0.72 in 2:1 Hex:EtOAc), the reaction mixture was diluted with ether/pentanes and filtered through a silica plug (Purification Method A). Evaporation of the solvent afforded 95 mg (0.85 mmol, 83% yield) of the title compound as a light pink oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.94 (d, *J* = 1, C*H*O), 7.78 (m, 2 H), 7.22 (dd, *J* = 3.6, 4.5, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 183.05 (*C*HO), 144.18, 136.33, 135.19, 128.39. Spectral properties are consistent with literature values.[5]

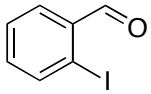


5-chloro-2-nitro-benzaldehdye. Using [$Cu(MeCN)_4$](PF_6). The reaction was run in a 20 mm culture tube open to air. Upon completion by TLC (R_f(aldehyde) = 0.82 and R_f(alcohol) = 0.36 in 2:1 Hex:EtOAc), the reaction mixture was diluted with 1:1 ether:pentanes and filtered through a silica plug (Purification Method A). Evaporation of the solvent afforded 175 mg (0.94 mmol, 94% y) of the title compound as a light pink solid (mp = 66 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.39 (s, 1 H, C*H*O), 8.11 (d, *J* = 1.8, 1 H,

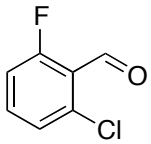
Ar), 7.95 (d, J = 8, Ar), 7.76 (dd, J = 8, 1.5, 1 H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 186.95 (*C*HO), 150.20, 140.36, 134.31, 131.05, 129.45, 124.94 Spectral properties are consistent with literature values.[23]



5-amino-2-chlorobenzaldehyde. Using $[Cu(MeCN)_4](PF_6)$. The reaction was run in a 20 mm culture tube open to air. Upon completion by TLC (1 h, R_f(aldehyde) = 0.77 and R_f(alcohol) = 0.23 in 1:1 Hex:EtOAc), the reaction mixture was diluted with 1:1 ether:pentanes and filtered through a silica plug (Purification Method A). Evaporation of the solvent afforded 151 mg (0.97 mmol, 96 % y) of the title compound as a yellow powder (mp = 270 °C, decomp.). ^{1}H NMR (300 MHz, DMSO-d_6): δ = 10.2 (s, 1 H, C*H*O), 7.22 (d, J = 8.5, 1 H, Ar), 7.03 (d, J = 3, 1 H, Ar), 6.84 (dd, J = 8.5, 3, 1 H, Ar), 5.61 (br s, 2 H, NH_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.48 (s, 1 H, C*H*O), 7.30 (s, J = 8.5, 1 H, Ar), 7.28 (d, J = 3. 1 H, Ar), 6.91 (dd, J = 8.5, 3, 1 H, Ar), 3.9 (br s, 2 H, NH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 190.25 (*C*HO), 145.72, 132.84, 131.27, 121.88, 114.26. Only 5 Aryl C's could be identified. Longer collection times or more concentrated samples led to decomposition, presumably imine formation. Spectral properties are consistent with literature values in DMSO-d_6.[24]



2-iodobenzaldehyde. Using $[Cu(MeCN)_4](BF_4)$. The reaction was run in a 20 mm culture tube open to air. Upon completion by TLC (1 h, R_f(aldehyde) = 0.89 and R_f(alcohol) = 0.64 in 2:1 Hex:EtOAc), the reaction mixture was diluted with EtOAc and filtered through a silica plug. Evaporation of the solvent afforded 227 mg (0.98 mmol, 96% y) of the title compound as a light brown oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.07 (d, J = 1, 1 H, C*H*O), 7.95 (dd, J = 7.8, 1.2, 1 H, Ar), 7.88 (dd, J = 7.5, 1.8, 1 H, Ar), 7.46 (t, J = 7.5, 1 H, Ar), 7.28 (td, J = 7.5, 2.1, 1 H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 195.63 (s, 1 H, C*H*O), 140.56, 135.39, 135.05, 130.18, 128.65, 100.63. Spectral properties are consistent with literature values.[25]



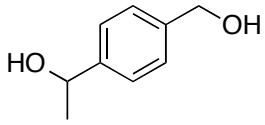
2-chloro-6-fluoro-benzaldehyde. Using $[Cu(MeCN)_4](BF_4)$. The reaction was run in a 20 mm culture tube open to air. Upon completion by TLC (1 h, R_f(aldehyde) = 0.79 and R_f(alcohol) = 0.64 in 2:1 Hex:EtOAc), the reaction mixture was diluted with EtOAC and filtered through a silica plug. Evaporation of the solvent afforded 162 mg (1.02 mmol, >98% y) of the title compound as a tan solid (mp 33-35 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.47 (s, 1 H, C*H*O), 7.49 (dt, J = 5.7, 8.1, 1 H, Ar), 7.27 (m, 1 H, Ar), 7.11 (t, J = 9.6, Ar). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 186.64 (d, $J_{C\text{-}F}$= 3, *C*HO), 163.02 (d, $J_{C\text{-}F}$ = 263, *C*F),

136.85 (d, $J_{C\text{-}F}$ = 3.6), 13.94 (d, $J_{C\text{-}F}$ = 10.6), 126.5, 121.61 (d, $J_{C\text{-}F}$ = 9.5), 115.45 (d, $J_{C\text{-}F}$ = 21.5). Spectral properties are consistent with literature values.[26]

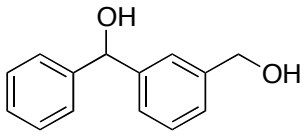
VI. Synthesis and Characterization of Diol Substrates.

1,5-hexanediol was purchased from Aldrich and used as received. All other diols were synthesized by reduction of the corresponding diketone, or ketone/carboxylic acid with $LiAlH_4$ in THF and purified by silica column chromatography (gradient elution with Hex:EtOAc). A representative procedure is given below.

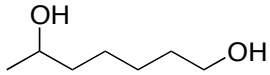
Representative Procedure for the Preparation of Diols. A solution of 5-benzoylpentanoic acid (1.03 g, 5.0 mmol) in THF (250 mL) was cooled to 0 °C under N_2. $LiAlH_4$ (1 g, 26 mmol) was added portionwise over 1h. The reaction was allowed to warm to room temperature overnight with stirring. The mixture was then cooled to 0 °C and quenched with the addition of ethyl acetate (~ 100 mL), and water (~ 150 mL). The layers were separated, and the aqueous layer extracted with EtOAc (2 x 100 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and the solvent evaporated. The crude material was purified by silica column chromatography (gradient elution of EtOAc in Hexanes, R_f values are given in Table S1) to yield diol **7** as a white solid (0.86 g, 4.4 mmol, 88% yield). Characterization data is given below.



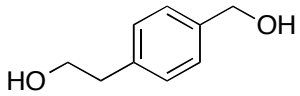
4-(1'-hydroxyethyl)benzyl alcohol (1). The title compound was obtained in 92 % (4.8 g, 31.5 mmol) as a white solid (mp 63-64 °C) according to the literature procedure.[3] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35 (m, 5 H, Ar), 4.90 (dq, *J* = 6.3, 3, 1 H, C*H*OH), 4.67 (d, *J* = 6, CH_2OH), 1.95 (d, *J* = 3, 1 H, O*H*), 1.84 (t, *J* = 6, 1 H, O*H*), 1.48 (d, *J* = 6.6, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.43, 140.25, 127.35, 125.77, 70.32, 65.22, 25.35. Spectral parameters are consistent with literature values.[3]



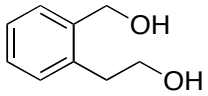
[3-(Hydroxylmethyl)phenyl]phenyl)methanol (2). The title compound was obtained according to the general procedure as a white solid (mp 102 °C). H NMR (300 MHz, $CDCl_3$): δ = 7.42-7.24 (m, 9 H, Ar), 5.85 (s, 1H, C*H*OH), 4.67(s, 2 H, CH_2OH), 2.3 (br s, 1 H, O*H*), 1.75 (br s, 1 H, O*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.32, 143.86, 141.30, 128.89, 128.69, 127.80, 126.68, 126.34, 126.00, 125.15, 76.35, 65.41. Spectral properties are consistent with literature values.[27]



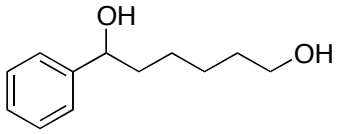
1,6-heptane diol (**3**). The title compound was obtained according to the general procedure as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.76 (m, 1 H, C*H*OH), 3.604 (t, *J* = 6.6, 2 H, CH_2OH), 1.93 (br s, 2 H, 2 O*H*), 1.55 (m, 2 H, CH_2), 1.47-1.31 (m, 6 H, 3 CH_2), 1.16 (d, *J* = 6.3, 3 H, CH_3).^{13}C NMR (75 MHz, $CDCl_3$): δ = 67.90, 62.55, 39.23, 32.65, 25.81, 25.55, 23.50. ^{1}H NMR (300 MHz, MeOD-d_4): δ = 4.86 (s, 2H. 2 O*H*), 3.71 (m, 1 H, C*H*OH), 3.54 (t, *J* = 6.6, 2 H, CH_2OH), 1.55 (m, 2 H, CH_2), 1.45-1.33 (m, 6 H, 3 CH_2), 1.15 (d, *J* = 6.3, 3 H, CH_3). Spectral properties are consistent with literature values.[28]



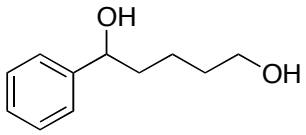
2-(4-Hydroxymethyl-phenyl)-ethanol (5). The title compound was obtained according to the general procedure as a white solid (mp = 64-65 °C). ^{1}H NMR (300 MHz, MeOD-d_4): δ = 7.28 (d, *J* = 8, 2 H, Ar), 7.20 (d, *J* = 8, 2 H, Ar), 4.85 (s, 2 H, 2 O*H*), 4.56 (s, 2 H, CH_2OH), 3.72 (t, *J* = 7.2, 2 H, CH_2OH), 2.81 (t, *J* = 7.2, 2 H, CH_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.33 (d, *J* = 7.8, 2 H, Ar), 7.24 (d, *J*= 7.8, 2 H, Ar), 4.67 (d, *J* = 5.7, 2 H, CH_2OH), 3.86 (dt, *J* = 6.3, 6.0, 2 H, CH_2OH), 2.87 (t, *J* = 6.3, 2 H, CH_2), 1.62 (br t, *J* = 5.1, 1 H, O*H*), 1.38 (br t, *J* = 5.1, 1 H, O*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.30, 138.21, 129.468, 127.595, 65.40, 63.87, 39.08. Spectral parameters are consistent with literature values.[29]



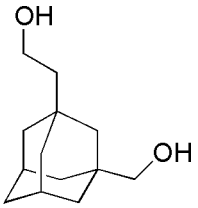
2-(2-hydroxymethyl-phenyl)-ethanol (6). The title compound was obtained according to the general proceudre as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.32-7.25 (m, 2 H, Ar), 7.24-7.17 (m, 2 H, Ar), 4.54 (s, 2 H, CH_2), 3.76 (t, *J* = 6, 2 H, CH_2OH), 3.7 (br, 1 H, O*H*), 3.1 (br s, 1 H, O*H*), 2.86 (t, *J* = 6, 2 H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.39, 138.33, 130.20, 129.92, 128.70, 26.88, 63.49, 63.23, 35.16. HRMS (ESI) [M+Na^+]/z calcd. 327.1565, found 327.1567.



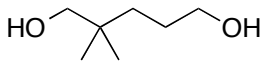
1-phenylhexane-1,6-diol (7). The title compound was obtained according to the general procedure as a white solid (mp 55-56 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36-7.25 (m, 5 H, Ar), 4.67 (m, 1 H, C*H*OH), 3.62 (dt, *J* = 6.3, 4.8, 2 H, CH_2OH), 1.91 (br s, 1 H O*H*), 1.76 (m, 2 H, CH_2), 1.63-1.24 (m, 7 H, 3 CH_2 and O*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.03, 128.60, 127.66, 126.03, 74.65, 62.93, 39.15, 32.73, 25.77, 25.72. Spectral properties are consistent with literature values.[28]



1-phenyl pentane-1,5-diol (8). The title compound was obtained according to the general procedure as a white solid (mp 54 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.33-7.24 (m, 5 H, Ar), 4.63 (dd, *J* = 7.8, 5.4, 1 H, C*H*OH), 3.56 (t, *J* = 6.3, 2 H, CH_2OH), 2.83 (br s, 1 H, O*H*), 2.33 (br s, 1 H, O*H*), 1.74 (m, 2 H, CH_2), 1.56 (m, 3 H, CH_2), 1.35 (m, 1 H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.93, 128.50, 127.53, 125.94, 74.42, 62.50, 38.74, 32.40, 22.07. Spectral properties are consistent with literature values.[28]



2-(3-Hydroxymethyl-adamantan-1-yl)-ethanol (**9**). The title compound was obtained according to the general procedure as a white solid (mp 66-69 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.72 (t, *J* = 7.5, 2 H, CH_2OH), 3.22 (s, 2 H, CH_2OH), 2.06 (m, 2 H, CH_2), 1.62-1.43 (m, 12 H), 1.29 (s, 2 H), 1.3-1.1 9 (br, 2 H, 2 O*H*).). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 73.62, 58.91, 46.93, 44.32, 42.41, 38.65, 36.69, 35.39, 32.40, 29.66. HRMS (EI) $[M\text{-}MeOH]^+$/z calcd. 179.1431, found 179.1427.



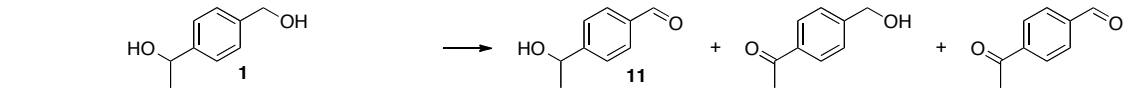
2,2-dimethyl-1,5-pentanediol (10). The title compound was obtained according to the general procedure as a colorless, viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.61 (t, *J* = 6.3, 2 H, CH_2OH), 3.30 (s, 2 H, CH_2OH), 1.52 (m, 2 H, CH_2), 2.6 (br s, 2 H, 2 O*H*) 1.29 (m, 2 H, CH_2), 0.86 (s, 6 H, 2 CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 71.21, 63.55, 34.93, 34.37, 27.03, 24.24. Spectral properties are consistent with literature values.[2]

VII. The Selective Oxidation of Unprotected Diols.

Screening procedure for selective diol oxidation. To a solution of alcohol (0.25 mmol) in CH_3CN (0.25 mL) in a 13 mm culture tube was added sequentially a solution of (1) Cu salt (0.25 mL, 0.05M), (2) bpy (0.25 mL, 0.05M), (3) TEMPO (0.25 mL, 0.05M), and (4) base additive (0.25 mL, 0.10M). The reaction mixture was stirred at room temperature open to air for 24 h. At regular time intervals, aliquots were taken, diluted with CH_2Cl_2 (3 mL), filtered through a plug of silica and analyzed by GC. These data are below.

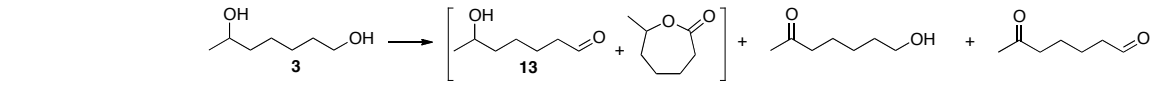
With some substrates (**5**, **6**, **9** and **10**) the parent Cu(OTf)/NMI catalyst proved to be effective. In other cases, focused screening of modified catalyst systems led to improved results. For these cases, see screening data below.

Selective Oxidation of 1° over 2° Benzylic Alcohols.



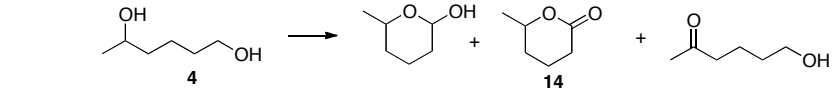
Cu Source	Base	1 h	6 h	1 h	6 h	1 h	6 h	1 h	6 h
Cu(OTf)	NMI	43%	30%	57%	35%	<1%	<1%	<1%	65%
CuBr	NMI	51%	<1%	49%	64%	<1%	<1%	<1%	36%
$Cu(OTf)_2$	NMI	98%	>98%	2%	<1%	<1%	<1%	<1%	<1%
$CuBr_2$	NMI	<1%	>98%	94%	<1%	<1%	<1%	6%	<1%
CuBr	DBU	47%	<1%	53%	82%	<1%	<1%	<1%	18%
$Cu(OTf)_2$	DBU	70%	<1%	22%	80%	<1%	<1%	7%	20%
$CuBr_2$	***DBU***	***29%***	***<1%***	***71%***	***71%***	***<1%***	***<1%***	***<1%***	***29%***

Selective Oxidation of 1° over 2° Aliphatic Alcohols.



Cu Source	Base	24 h	24 h	24 h	24 h
Cu(OTf)	NMI	<1%	97%	<1%	2%
CuBr	***NMI***	***8%***	***90%***	***<1%***	***2%***
$Cu(OTf)_2$	NMI	83%	14%	3%	<1%
$CuBr_2$	NMI	96%	3%	1%	<1%
CuBr	DBU	94%	2%	3%	1%
$Cu(OTf)_2$	DBU	94%	1%	3%	2%
$CuBr_2$	DBU	94%	3%	3%	<1%

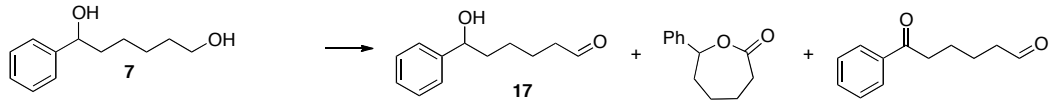
Lactone and aldehyde **13** are indistinguishable by GC, but upon workup and purification Cu(OTf)/NMI was found to yield more lactone than CuBr/NMI.



Cu Source	Base	24 h	24 h	24 h	24 h
Cu(OTf)	***NMI***	***14%***	***1%***	***85%***	***<1%***
CuBr	NMI	14%	49%	37%	<1%
$Cu(OTf)_2$	NMI	84%	15%	1%	<1%
$CuBr_2$	NMI	16%	52%	32%	<1%
CuBr	DBU	70%	25%	5%	<1%
$Cu(OTf)_2$	DBU	65%	28%	7%	<1%
$CuBr_2$	DBU	62%	31%	6%	<1%

Selective Oxidation of 1° Aliphatic over 2° Benzylic Alcohols.

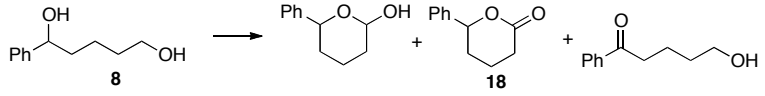
diol	aldehyde product	lactone	over oxidation



Cu Source	Base	6 h	6 h	6 h	6 h
Cu(OTf)	NMI	2%	59%	6%	33%
CuBr	***NMI***	***10%***	***70%***	***3%***	***17%***
$Cu(OTf)_2$	NMI	94%	6%	<1%	<1%
$CuBr_2$	NMI	>98%	<1%	<1%	<1%
CuBr	DBU	93%	4%	<1%	3%
$Cu(OTf)_2$	DBU	79%	13%	<1%	8%
$CuBr_2$	DBU	82%	10%	<1%	8%

Ketone product was observed in <1% yield in all cases.

diol	aldehyde product	ketone product



Cu Source	Base	24 h	24 h	24 h	24 h
Cu(OTf)	***NMI***	***3%***	***19%***	***67%***	***3%***
CuBr	NMI	22%	40%	29%	5%
$Cu(OTf)_2$	NMI	87%	10%	<1%	2%
$CuBr_2$	NMI	89%	9%	<1%	2%
CuBr	DBU	90%	1%	<1%	1%
$Cu(OTf)_2$	DBU	74%	1%	6%	3%
$CuBr_2$	DBU	61%	27%	6%	5%

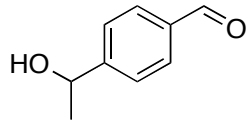
Only small amounts (<5%) of ketone/aldehdye overoxidation product was formed in each case.

Representative Procedure for the Selective Oxidation of Diols. To a solution of alcohol (1 mmol) in dry CH_3CN, (1 mL) in a 20 mm culture tube were added the following solutions: (1) Cu salt (0.05 mmol in 1 mL CH_3CN) (2) 2,2'-dipyridyl (0.05 mmol in 1 mL CH_3CN) (3) TEMPO (0.05 mmol in 1 mL CH_3CN) (4) base (0.1 mmol in 1 mL CH_3CN). The reaction mixture was stirred rapidly open to air and monitored by TLC (see Table S1) until no starting material remained. Preliminary studies indicate that the reactions described here are not subject to mass transfer effects, and rate of mixing and stir bar shape does not have a significant impact on the outcome of the reaction.

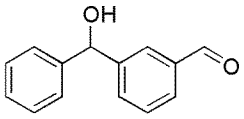
Workup Method A.
The reaction mixture was then neutralized with 1 N HCl and diluted with water (~10 mL) and extracted with dichloromethane (3 x 20 mL). The combined organics were washed with brine, dried over Na_2SO_4, and concentrated. The crude product was purified by silica column chromatography (gradient elution of EtOAc in Hex).

Workup Method B.
The crude reaction mixture was concentrated and purified by silica column chromatography (gradient elution of EtOAC in Hex).

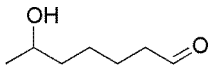
VIII. Characterization Data of Aldehyde/Alcohol Products.



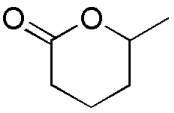
4-(1-hydroxyethyl)benzaldehyde (11). Using $CuBr_2$/DBU. The reaction reached completion in 1.5 h. Using workup method B, the title compound was obtained as a white solid (mp = 104-107 °C) in 95% y (142 mg, 94.6 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.96 (s, 1 H, C*H*O), 7.84 (d, *J* = 8.4, 2 H, Ar), 7.53 (d, *J* = 8.1, 2 H, Ar), 4.92 (quart, *J* = 6.3, 1 H, C*H*OH), 2.1 (br s, 1 H, O*H*), 1.49 (d, *J* = 6.3, 3 H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 192.24 (*C*HO), 152.99, 135.53, 130.09, 126.00, 69.87, 25.39. The spectroscopic data are consistent with those reported in the literature.[30]



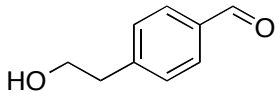
3-formylbenzhydrol (12). Using $CuBr_2$/NMI. The reaction reached completion in 24 h. Using workup method B, the title compound was obtained as a colorless oil in 88% yield (0.1 9g, 0.87 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.99 (s, 1 H, C*H*(O), 7.92 (s, 1 H), 7.78 (dd, *J*= 7.5, 1.5, 1 H), 7.67 (dm, *J* = 7.5, 1 H), 7.50 (t, *J* = 7.8, 1 H), 7.38-7.28 (m, 5H, Ph), 5.92 (d, *J* = 2.1, 1 H, C*H*), 2.41 (br s, 1 H, O*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 192.41 (*C*H(O), 145.05, 136.39, 136.71, 132.63, 129.33, 128.98, 128.93, 128.21, 127.77, 126.75, 75.88 (*C*HOH). Spectral data are consistent with literature parameters.[31]



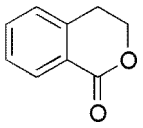
6-hydroxy-heptanal (13). Using CuBr/NMI. The reaction reached completion in 2 h. Using workup method B, the title compound was obtained as a colorless oil in 71% y (93 mg, 0.71 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.74 (dd, *J*=1.5, 2.7 Hz, 1 H, C(O)*H*), 3.77 (m, 1 H, C*H*), 2.43 (t, 2 H, CH_2CO), 1.74 (br s, 1 H, O*H*), 1.63 (m, 2 H, CH_2), 1.4-1.2 (m, 4H, 2 CH_2), 1.16 (d, *J* = 5.4 Hz, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$):): δ = 202.81 (*C*HO), 67.82, 43.93, 39.00, 25.40, 23.69, 23.65, 22.09. HRMS (TOF) [M^+]/z calcd. 283.1880, found 283.1877.



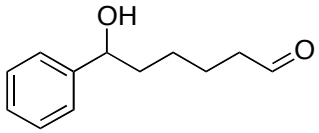
6-methyl-tetrahydro-pyran-2-one (14). Using [Cu(MeCN)$_4$](OTf)/NMI. The reaction reached completion in 24 h. Using workup method A, the title compound was obtained as a colorless oil in 84% y (101 mg, 0.89 mmol). ^{1}H NMR (300 MHz): δ = 4.44 (m, 1 H, C*H*), 2.56 (m, 1 H, CH_2), 2.44 (m, 1 H, CH_2), 1.97-1.79 (m, 3 H, CH_2), 1.52 (m, 1 H, CH_2), 1.38 (d, *J* = 1.5, 3 H, *C*H$_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.99 (*C*HO), 77.10, 29.79, 29.41, 21.89, 18.74. Spectral data are consistent with literature parameters.[32]



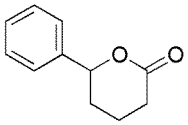
4-(2-hydroxyethyl)benzaldehyde (15). Using [Cu(MeCN)$_4$](OTf)/NMI. The reaction reached completion in 2.5 h. Using workup method B, the title compound was obtained as a colorless oil in 91% y (105 mg, 0.70 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.98 (s, 1 H, C*H*(O)), 7.83 (d, *J* = 8.1, 2 H, Ar), 7.41 (d, *J* = 8.1, 2 H, Ar), 3.92 (t, *J* = 6.6, 2H, CH_2OH), 2.96 (t, *J* = 6.6, 2H, CH_2), 2.2 (br s, 1 H, O*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 192.27 (*C*O), 146.51, 134.69, 129.98, 129.71, 62.87, 39.24. Spectral data are consistent with literature parameters.[33]



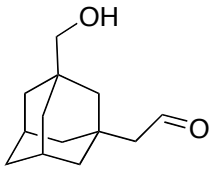
isochroman-1-one (16). Using [Cu(MeCN)$_4$](OTf)/NMI. The reaction reached completion in 4.5 h. Using workup method B, the title compound was obtained as a colorless oil in 82% y (120 mg, 0.81 mmol). ^{1}H NMR (300 MHz): δ = 8.09 (d, *J* = 7.8, 1 H, Ar), 7.54 (td, *J* = 7.8, 1.5, 1 H, Ar), 7.39 (t, *J* = 7.2, 1 H, Ar), 7.26 (d, *J* = 7.5), 4.54 (t, *J* = 6, 2 H, CH_2O), 3.06 (t, *J* = 6, 2 H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.28 (*C*O), 139.67, 133.78, 130.43, 127.76, 127.35, 125.35, 67.42, 27.89. Spectral data are consistent with literature values.[34]



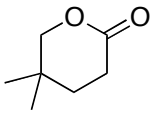
6-hydroxy-6-phenyl-hexanal (17). Using CuBr/NMI. The reaction reached completion in 3.5 h. Using workup method B, the title compound was obtained as a colorless oil in 62% y (118 mg, 0.62 mmol). ^{1}H NMR (300 MHz): δ = 9.61 (t, *J* = 1.8, 1 H, C*H*O), 7.23 (m, 5 H, Ar), 4.54 (t, *J* = 6.6. 1 H, C*H*OH), 2.30 (td, *J* = 7, 1.5, 2 H, CH_2), 2.1 (br s, 1 H, O*H*), 1.76-1.47 (m, 4 H, 2 CH_2), 1.43-1.13 (m, 2 H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ= 202.88 (*C*HO), 144.84, 128.55, 127.63, 125.96, 74.32, 43.86, 38.82, 25.44, 22.00. HRMS (TOF EI) $[M+Na]^+$/z calcd. 215.1043, found 215.1041.



6-phenyl-tetrahydro-2*H*-pyran-2-one (18). Using [Cu(MeCN)$_4$](OTf)/NMI. The reaction reached completion in 24 h. Using workup method B, the title compound was obtained as a white solid (mp = 61-62°C) in 88 % y (153 mg, 0.87 mmol). ^{1}H NMR (300 MHz): δ = 7.36 (m, 5H, Ar), 5.37 (dd, *J* = 10.5, 3.3, 1 H, C*H*), 2.72-2.55 (m, 2H, CH_2), 2.16 (m, 1 H, CH_2), 2.02-1.86 (m, 3H, 2CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.32 (*C*O), 139.75, 128.51, 128.16, 125.66, 81.55, 30.41, 29.42, 18.50. Spectral data are consistent with literature values.[35]

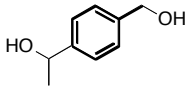
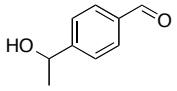
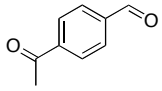
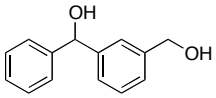
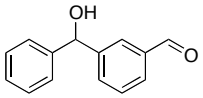
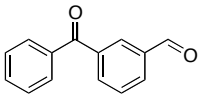
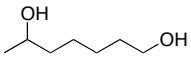
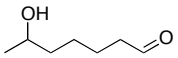
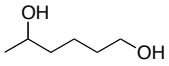
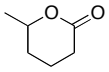
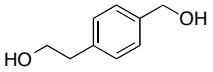
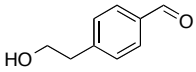
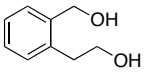
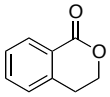
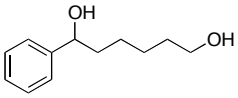
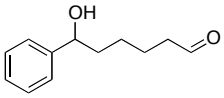
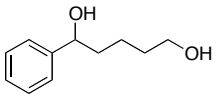
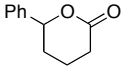
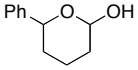
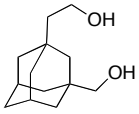
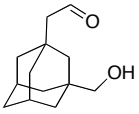
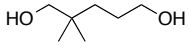
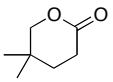
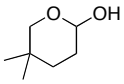


(3-hydroxymethyl-adamantan-1-yl)-acetaldehdye (19). Using $[Cu(MeCN)_4](OTf)$/NMI. The reaction reached completion in 2.5 h. Using workup method B, the title compound was obtained as a colorless oil in 98% y (209 mg, 1.0 mmol). ^{1}H NMR (300 MHz): δ = 9.86 (t, *J* = 3.5, 1 H, C*H*O), 3.23 (s, 2 H, CH_2), 2.17 (d, *J* =3.5, CH_2CHO), 2.09 (m, 2 H, CH_2), 1.7-1.4 (m, 12 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 203.59 (*C*HO), 73.38, 57.08, 44.39, 42.46, 38.40, 36.40, 35.58, 33.89, 28.62. HRMS (TOF EI) $[M+Na]^+$/z calcd. 231.1356, found 231.1352.



tetrahydro-5,5-dimethyl-2*H*-pyran-2-one (20). Using $[Cu(MeCN)_4](OTf)$/NMI. The reaction reached completion in 7 h at 50 °C. Using workup method B, the title compound was obtained as a white solid (mp 72-75 °C) in 93 % y (117 mg, 0.911 mmol). ^{1}H NMR (300 MHz): δ = 3.92 (s, 2 H, CH_2), 2.50 (t, *J* = 7.5, 2 H, CH_2), .65 (t, *J* = 7.5, 2 H, CH_2), 1.00 (s, 6 H, 2 CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.47 (*C*HO), 78.83, 32.99, 29.48, 27.35, 24.91. Spectral data are consistent with literature values.[36]

Table S2. R_f Values for Diols **1-10**, Alcohol/Aldehyde Products **11-20**, and Other Oxidation Products.

	Diol	R_f		Aldehyde Product	R_f	Other Oxidation Products		Solvent
1		0.31	**11**		0.63		0.88	1:1 H:EtOAc
2		0.16	**12**		0.42		0.59	2:1 H:EtOAc
3		0.53	**13**		0.52			100% EtOAc
4		0.18	**14**		0.44			2:1 H:EtOAc
5		0.19	**15**		0.44			1:1 H:EtOAc
6		0.21	**16**					2:1 H:EtOAx
7		0.29	**17**		0.78			1:1 H:EtOAc
8			**18**		0.65		0.83	1:1 H:EtOAc
9		0.16	**19**		0.64			1:1 H:EtOAc
10		0.19	**20**		0.64		0.63	1:1 H:EtOAc

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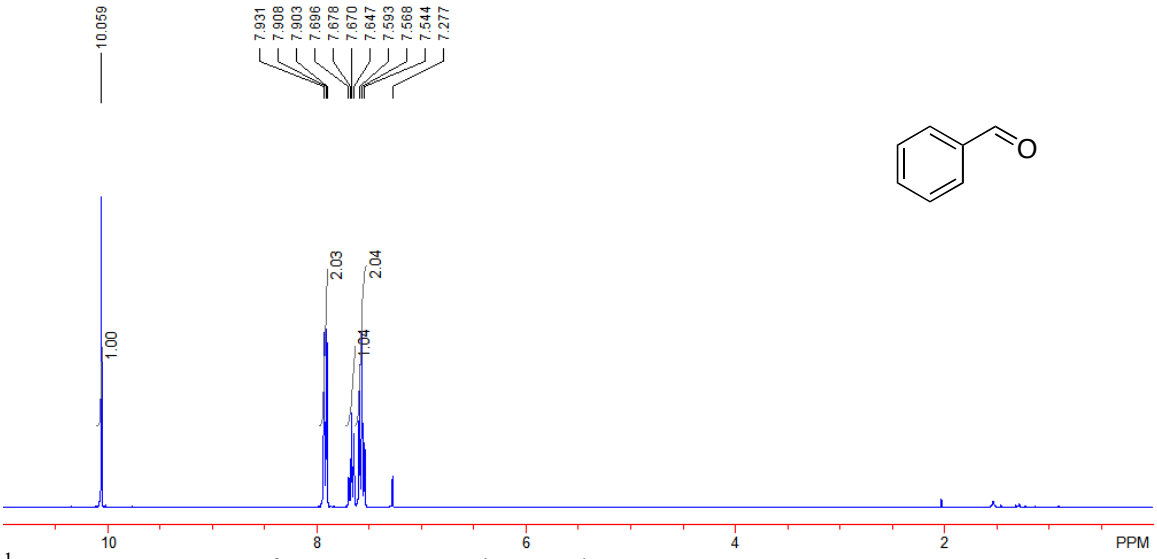
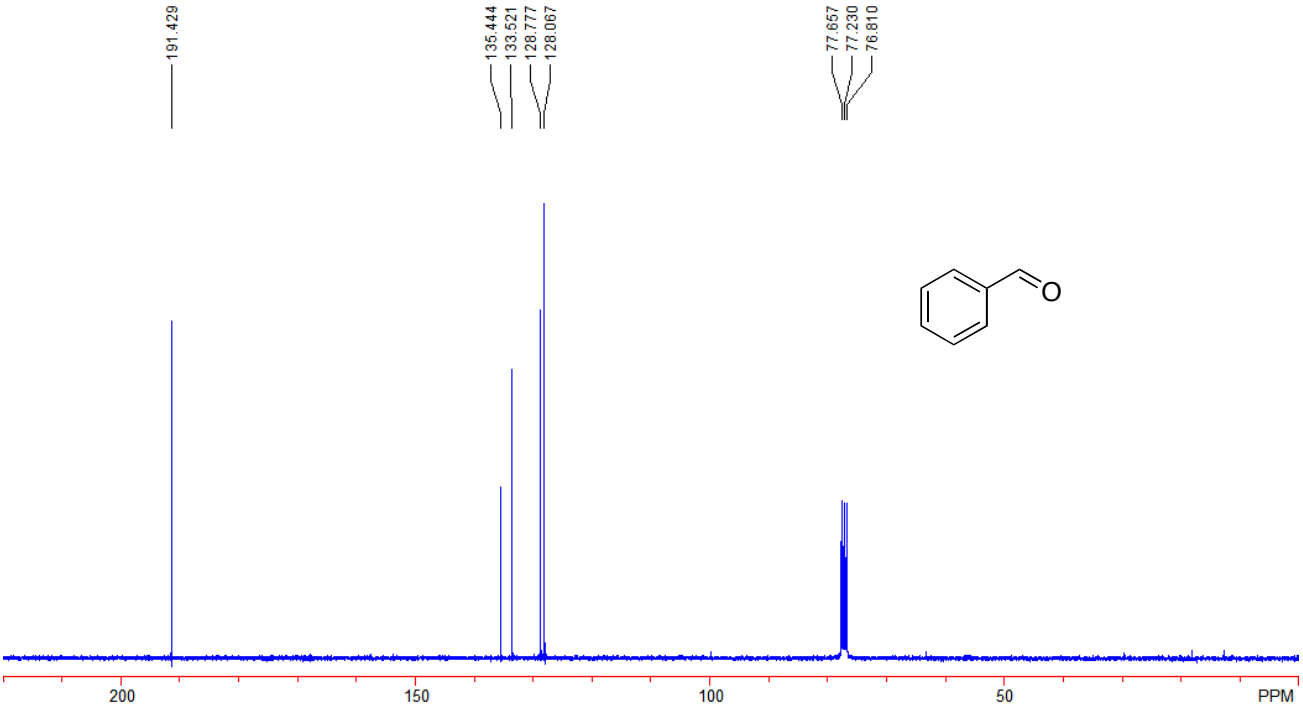
IX. ^{1}H and ^{13}C NMR spectra of Aldehyde Products.



^{1}H NMR spectrum of **benzaldehyde** in $CDCl_3$.



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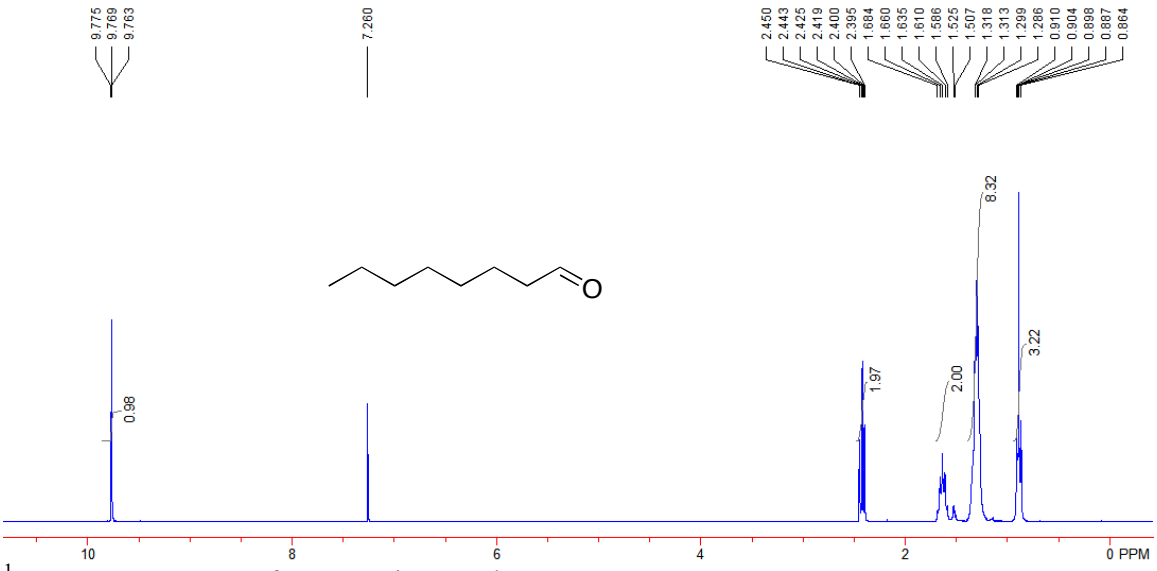
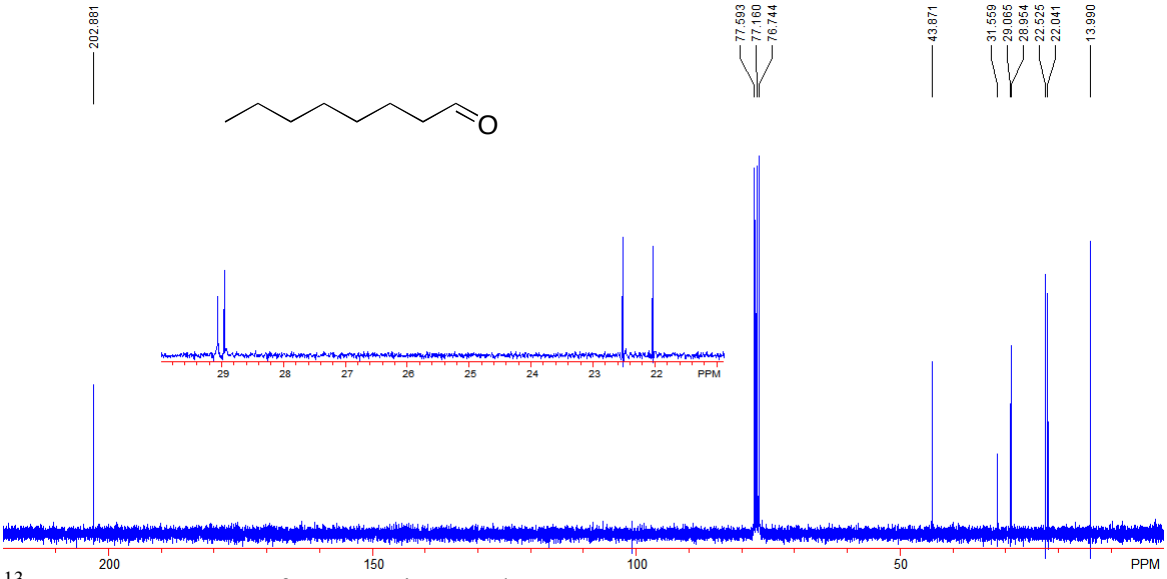


^{1}H NMR spectrum of **octanal** in $CDCl_3$.



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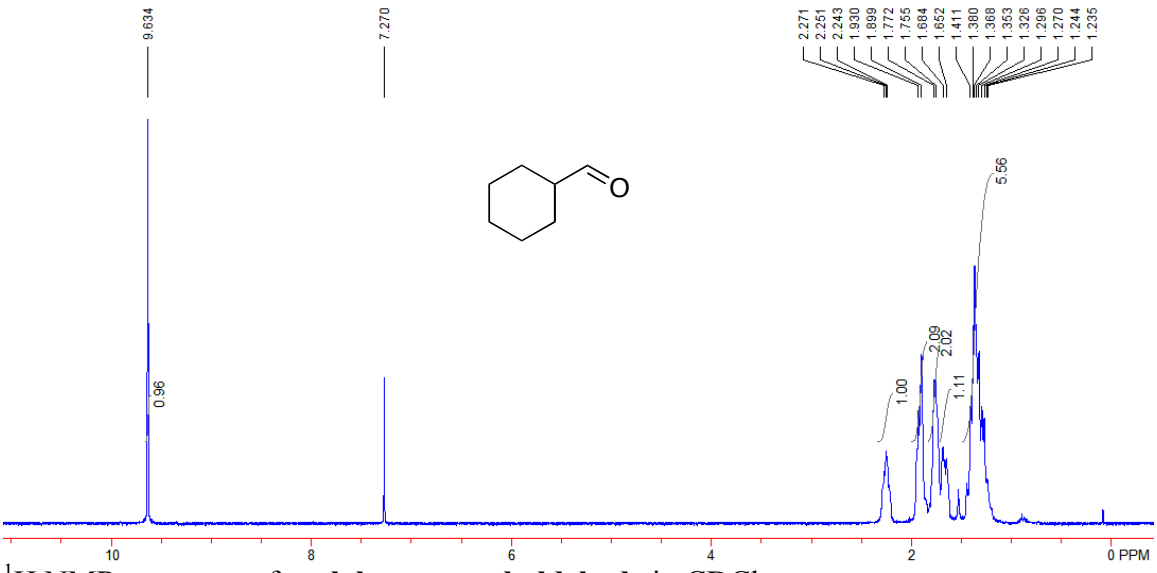
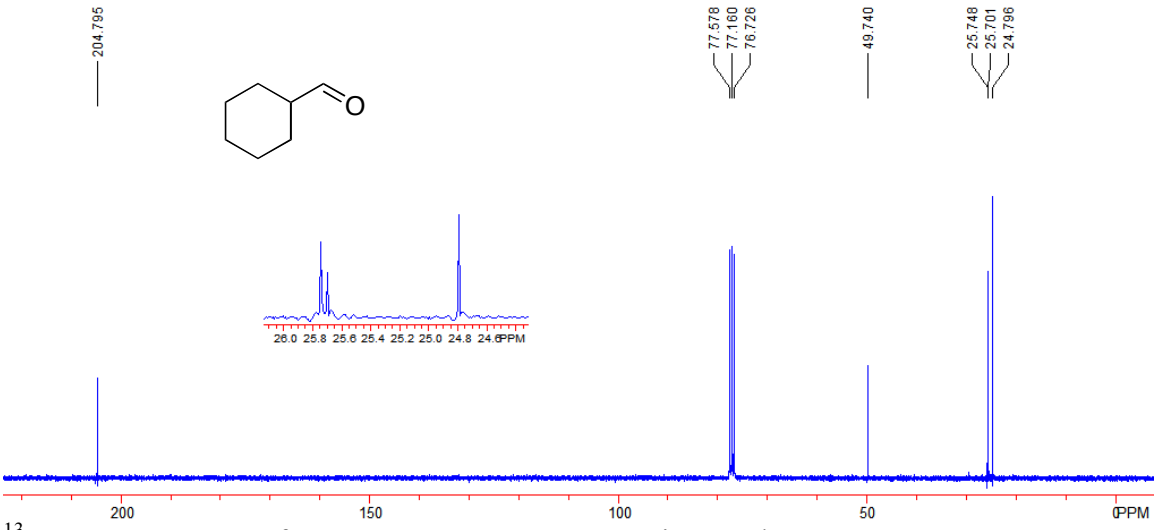


^{1}H NMR spectrum of **cyclohexane carbaldehyde** in $CDCl_3$.



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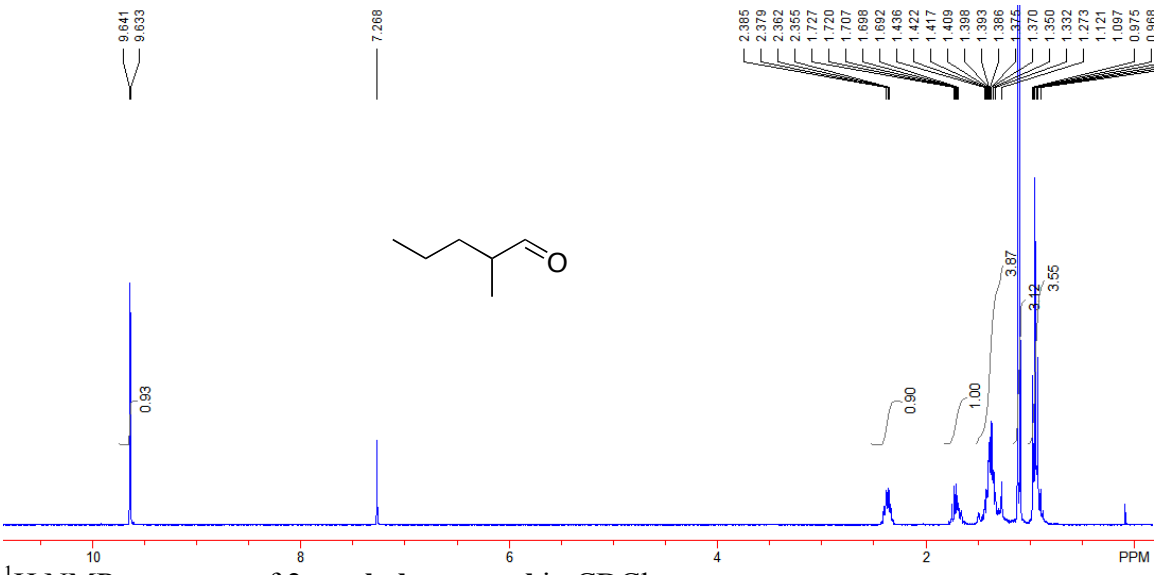
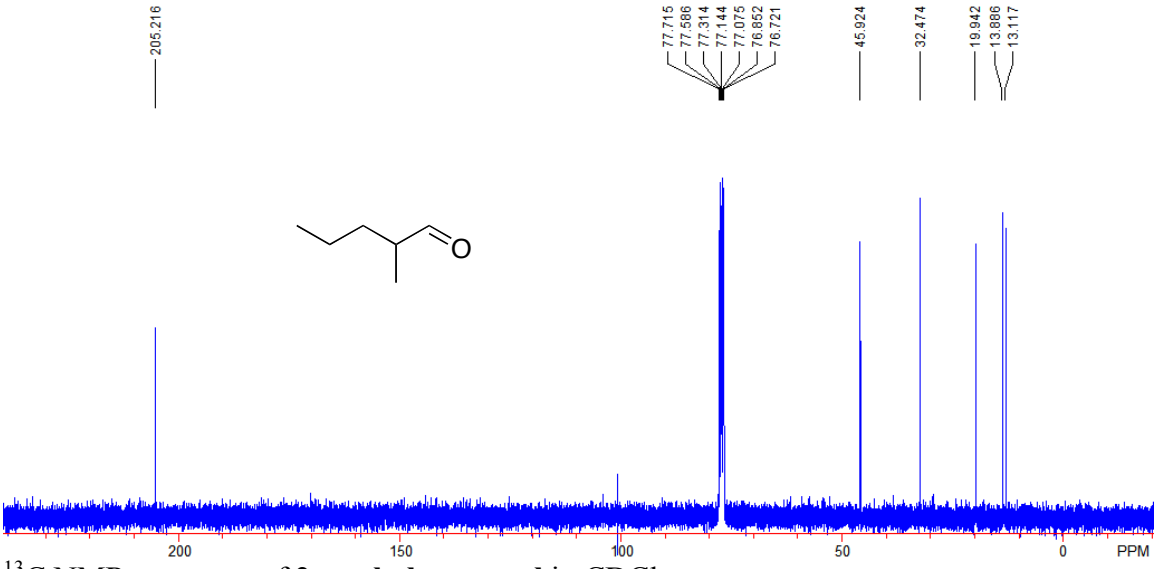


^{1}H NMR spectrum of **2-methyl pentanal** in $CDCl_3$.



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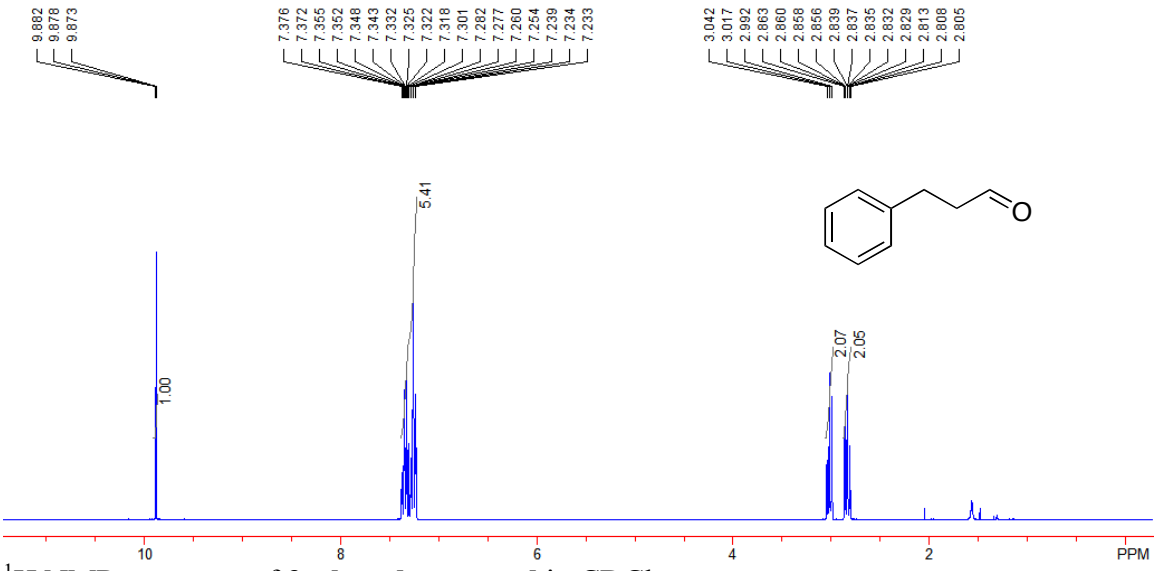
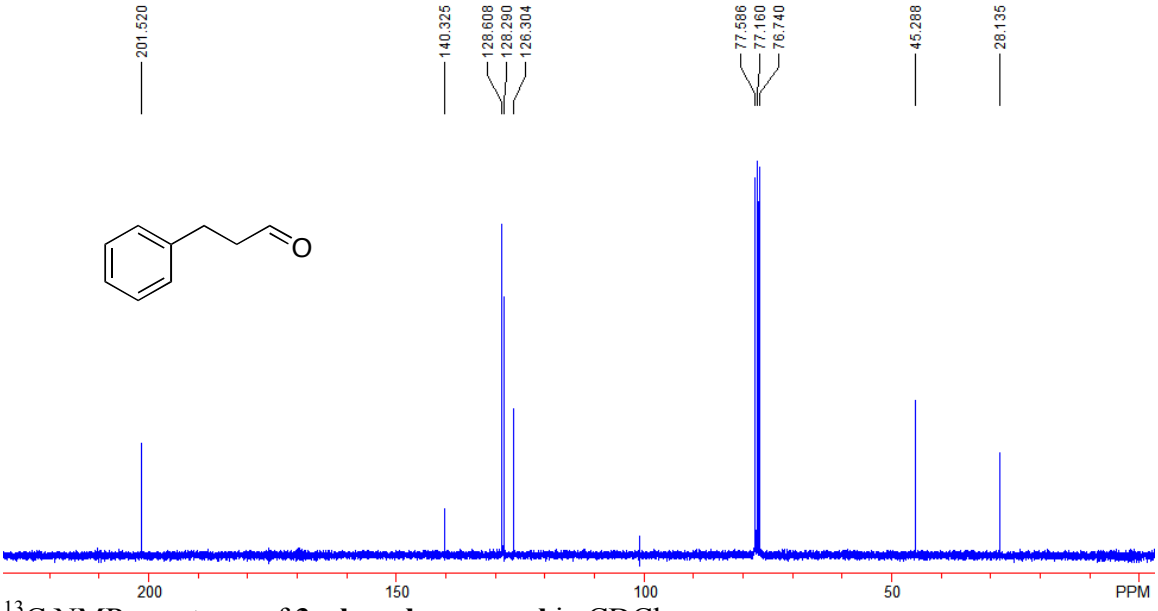


^{1}H NMR spectrum of **3-phenyl propanal** in $CDCl_3$.



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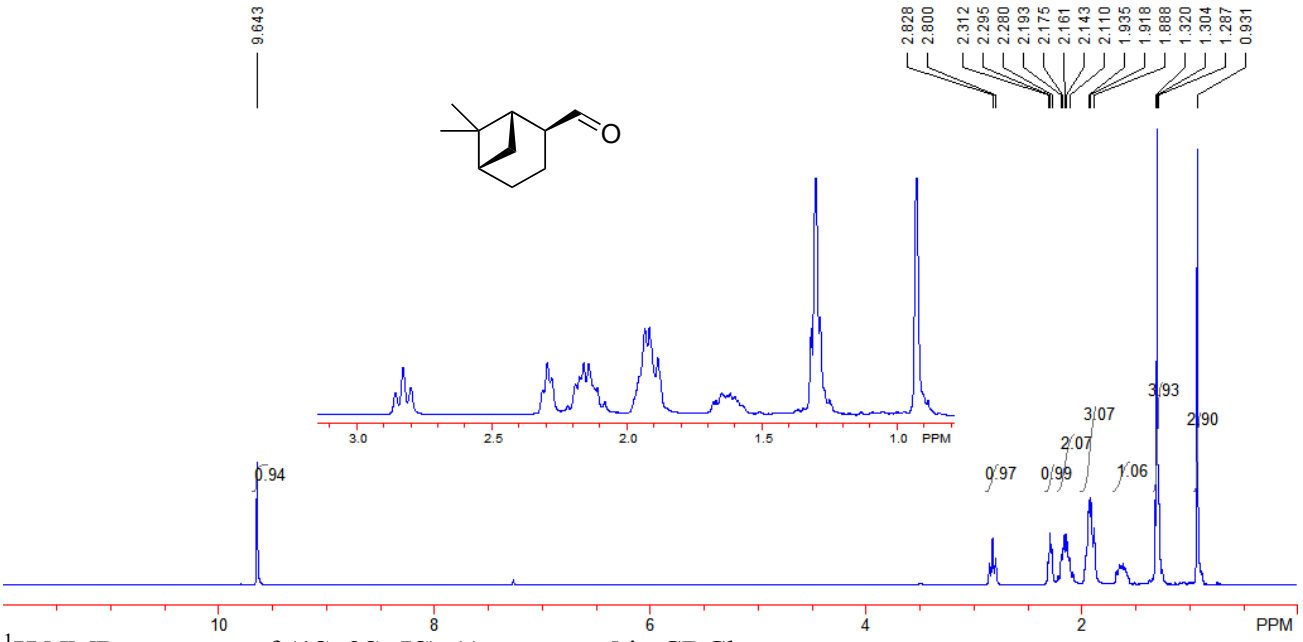
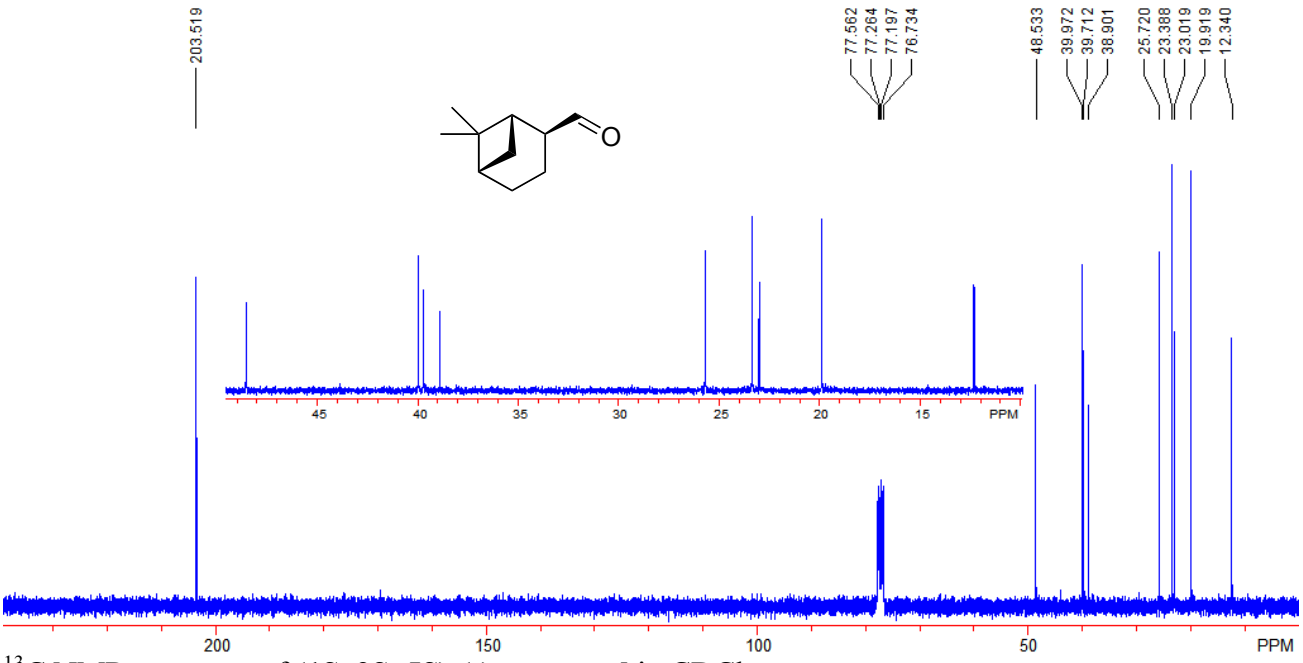


^{1}H NMR spectrum of **(1S, 2S, 5S)-(-)-myrtanal** in $CDCl_3$.



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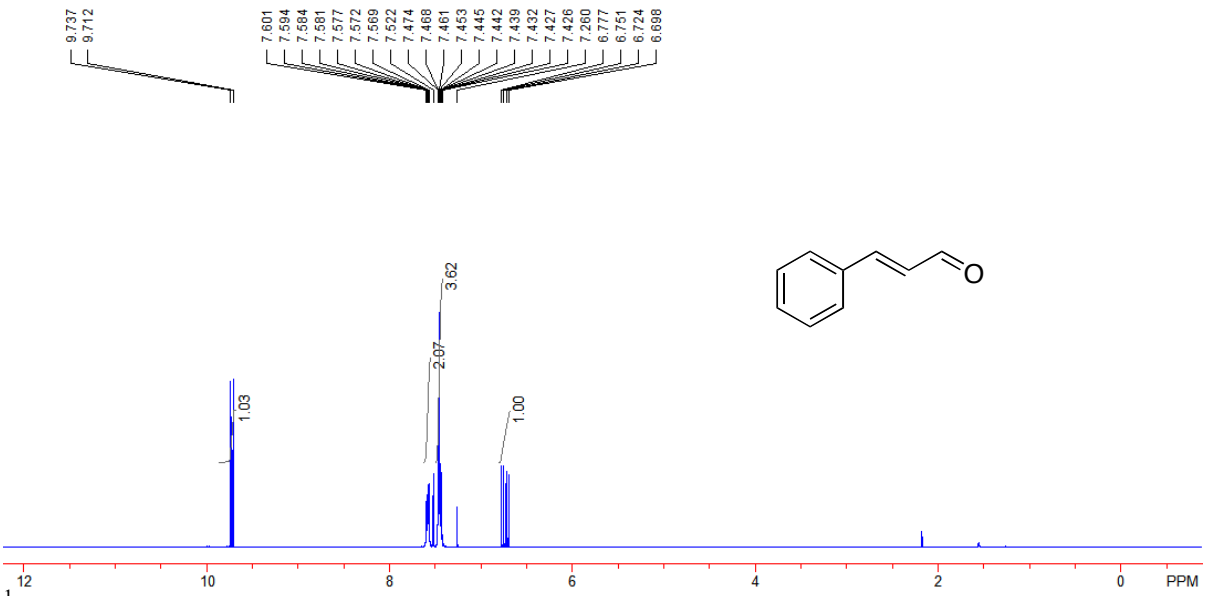

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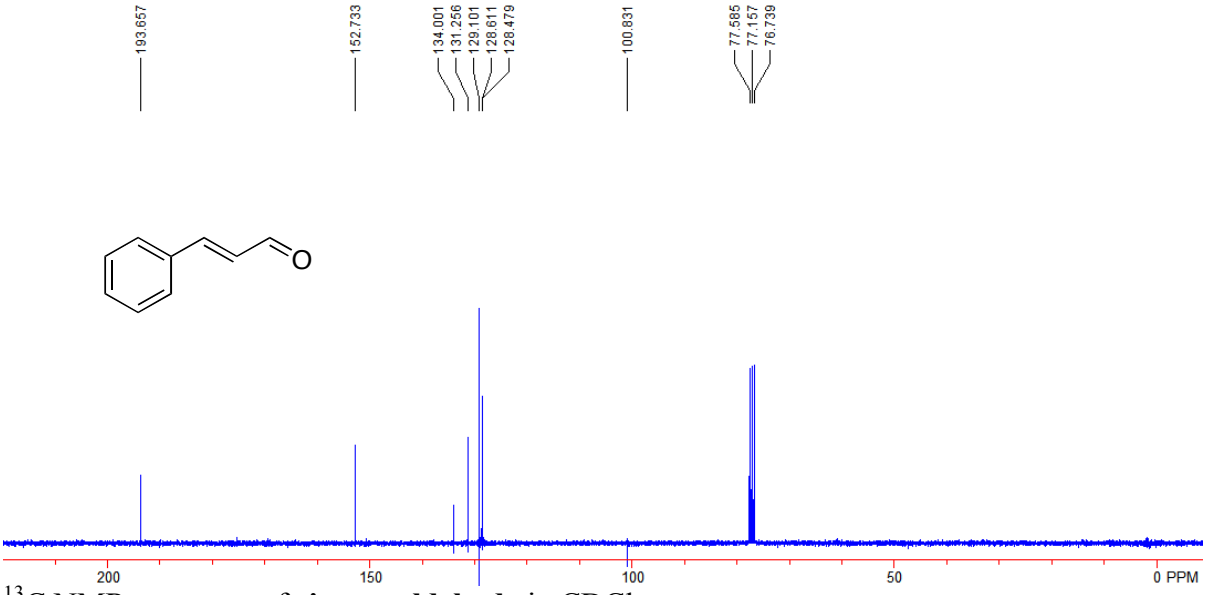
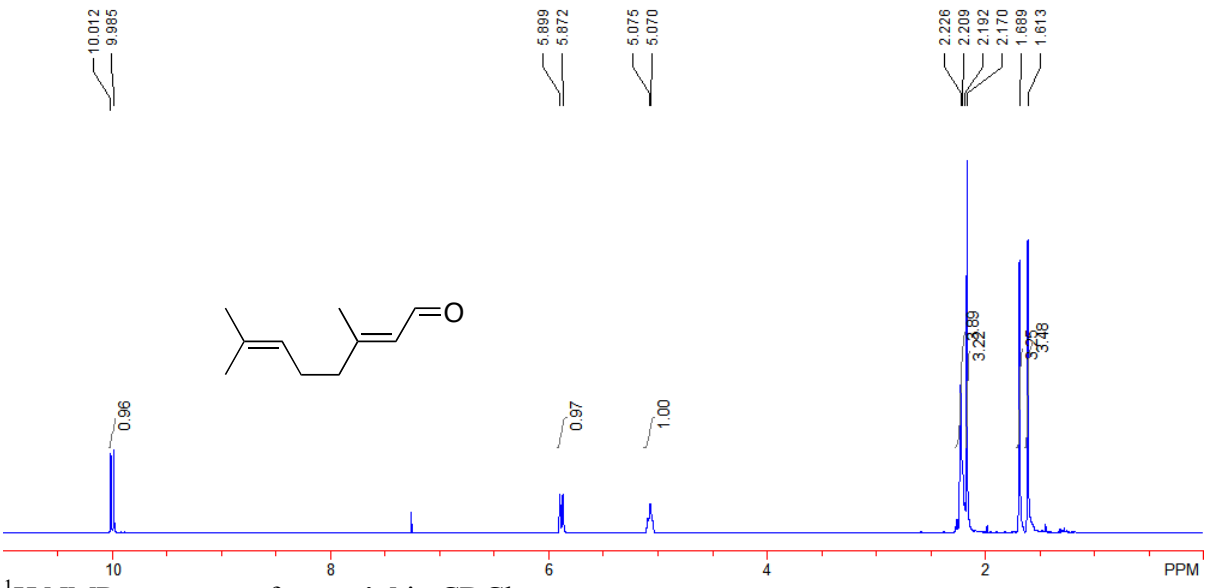


^{13}C NMR spectrum of **cinnamaldehyde** in $CDCl_3$.



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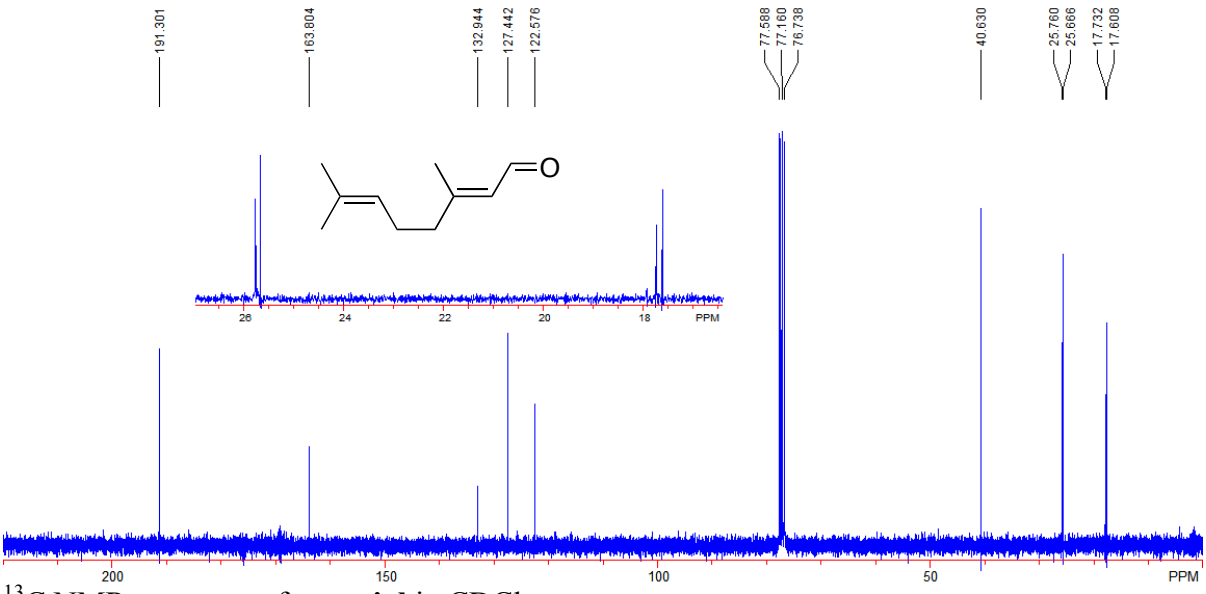
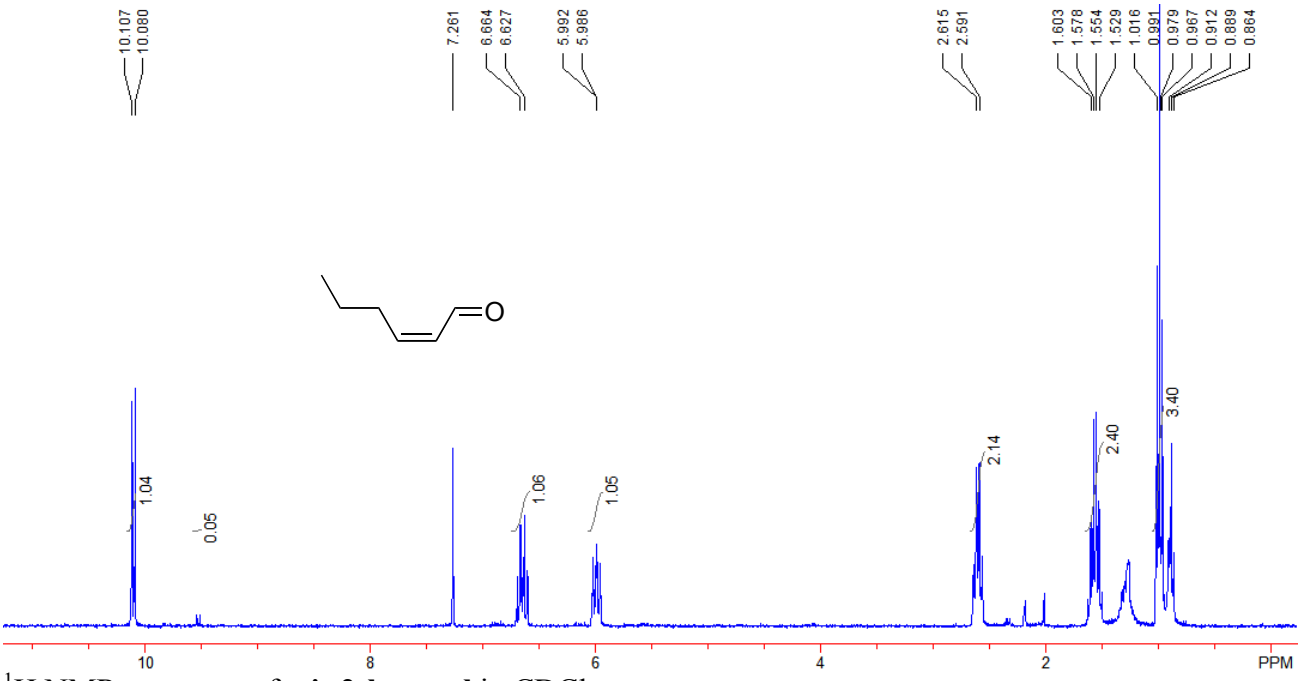
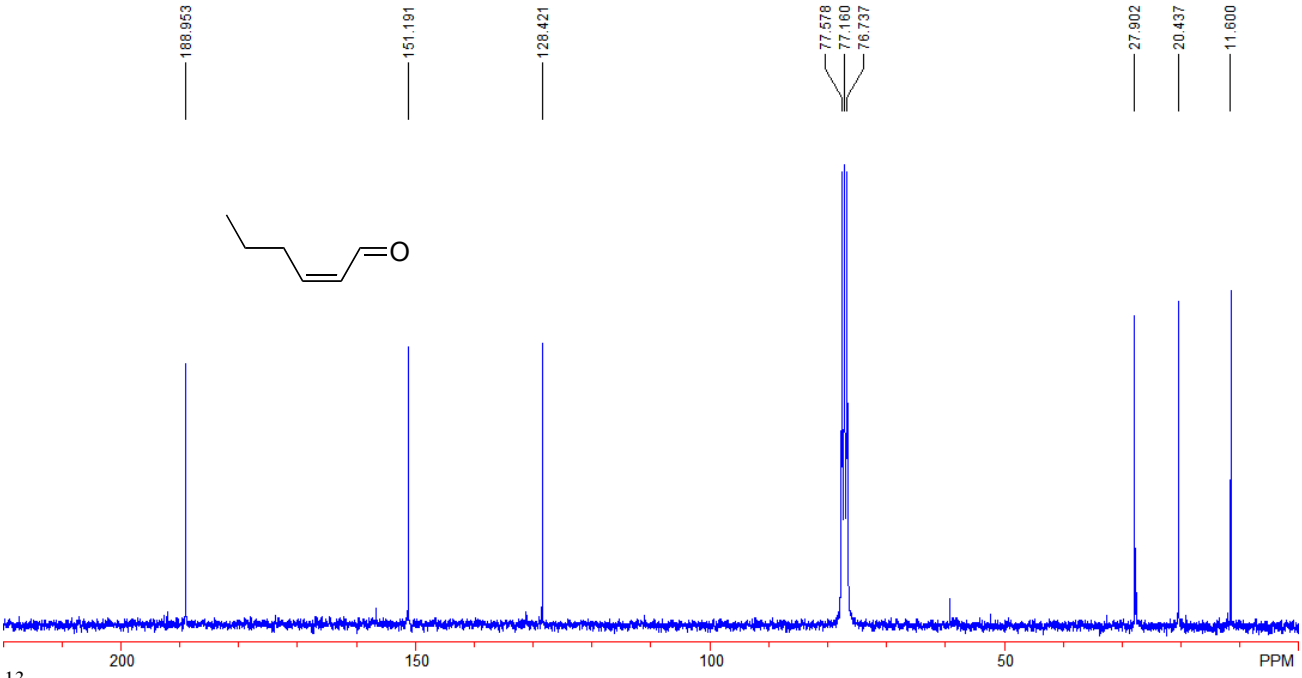


^{13}C NMR spectrum of **geranial** in $CDCl_3$.



^{1}H NMR spectrum of ***cis*-2-hexenal** in $CDCl_3$.



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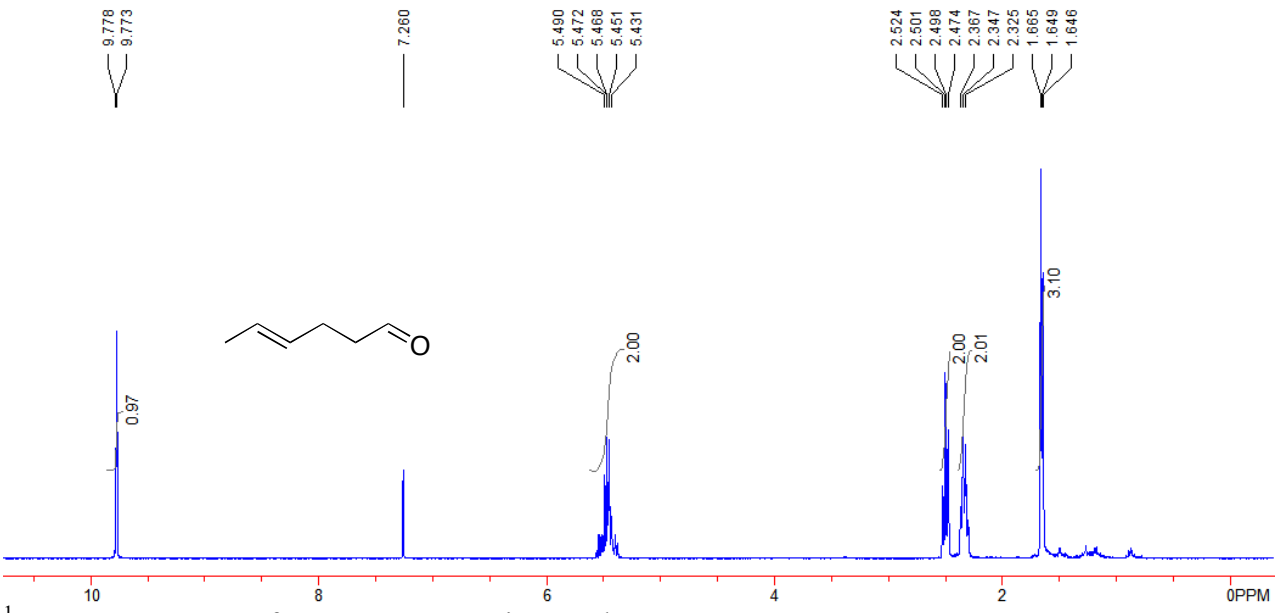
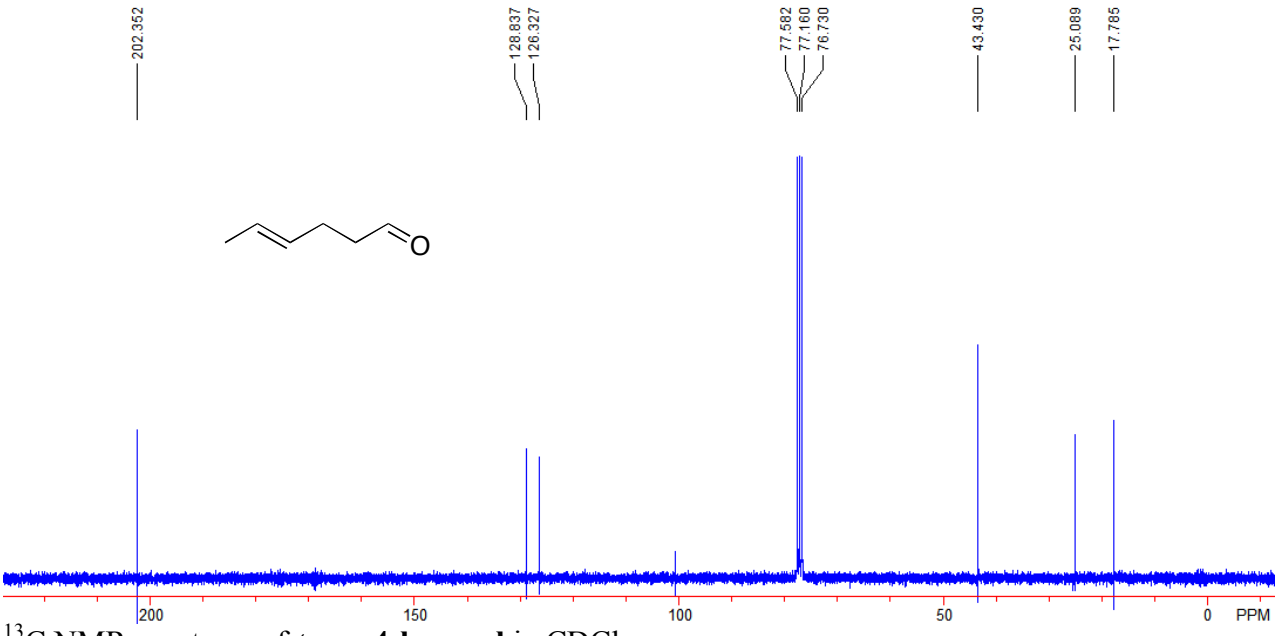
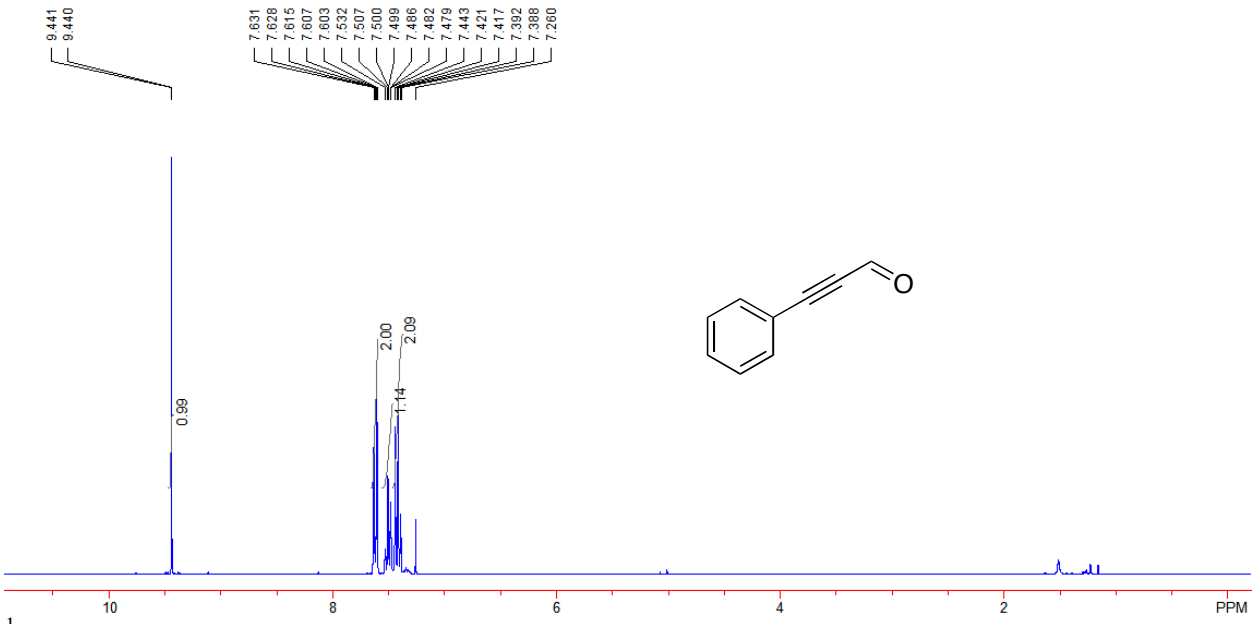


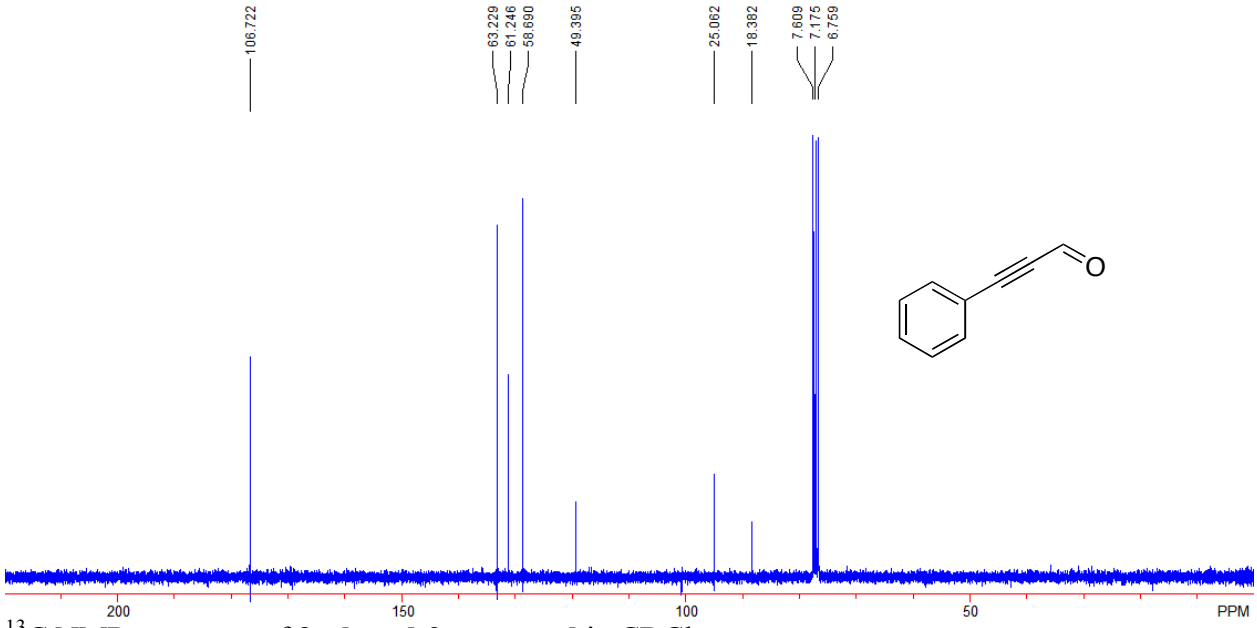
^{1}H NMR spectrum of ***trans*-4-hexenal** in $CDCl_3$.



^{13}C NMR spectrum of ***trans*-4-hexenal** in $CDCl_3$.



^{1}H NMR spectrum of **3-phenyl-2-propynal** in $CDCl_3$.



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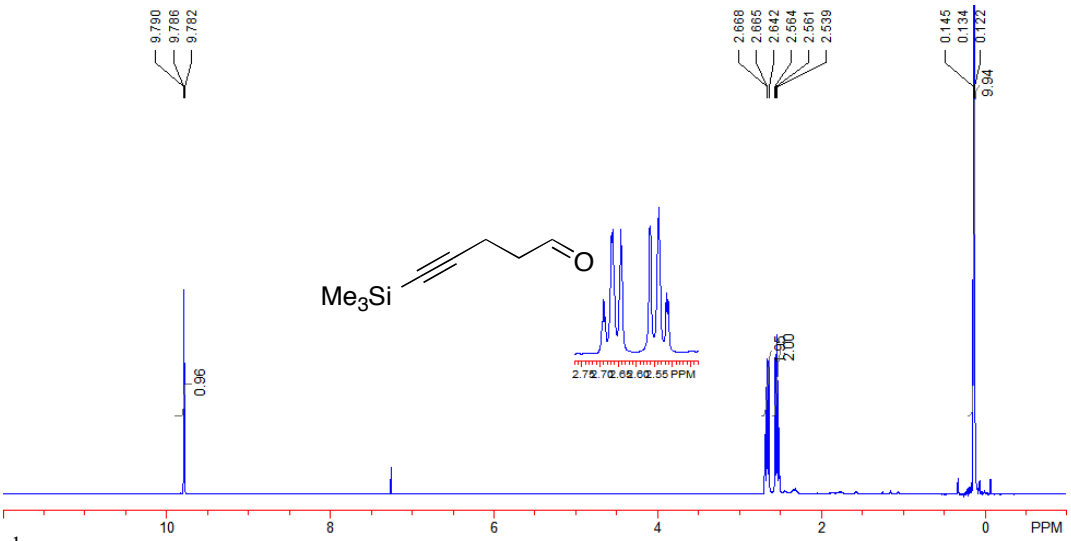
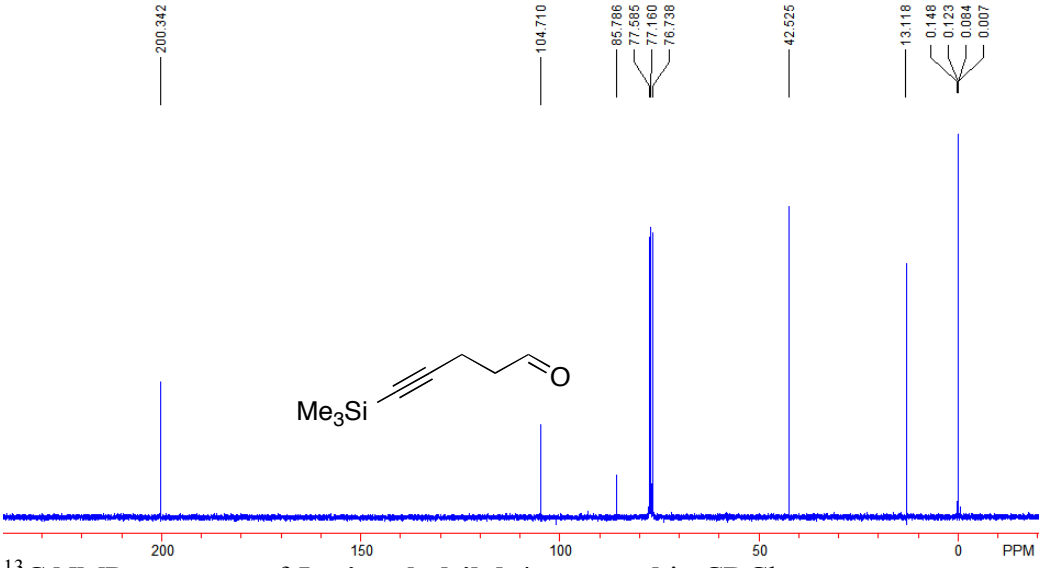


^{1}H NMR spectrum of **5-trimethylsilyl-4-pentynal** in $CDCl_3$.



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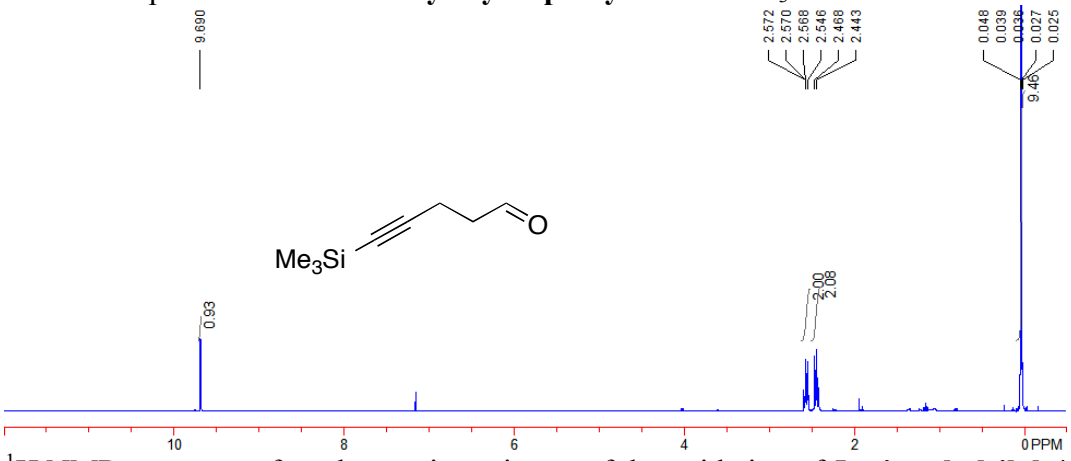
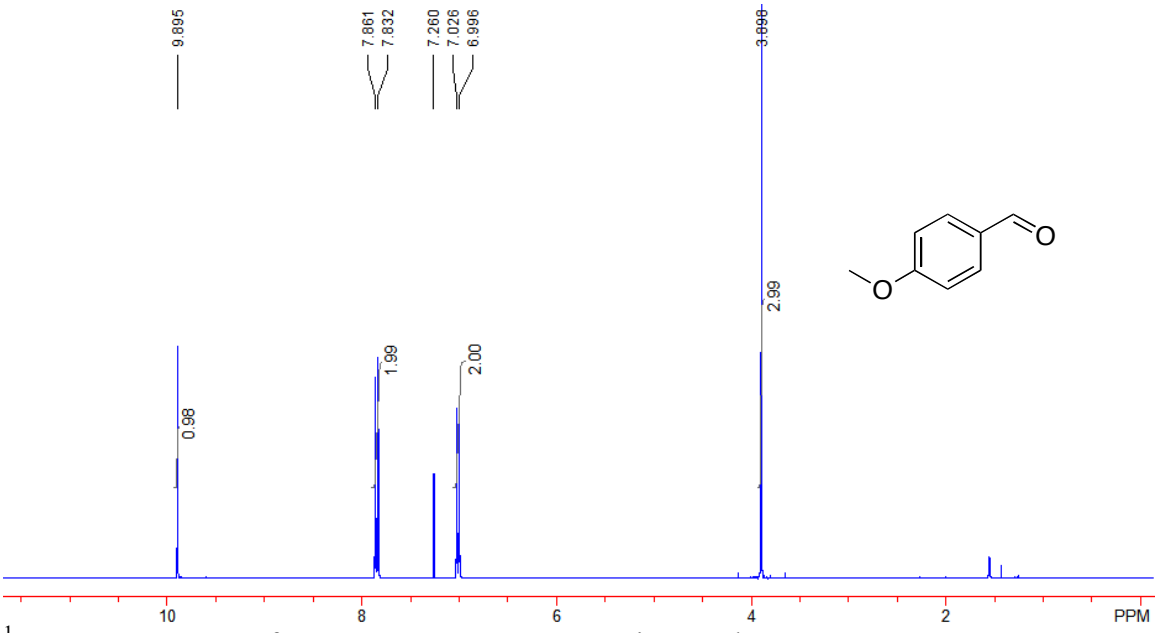
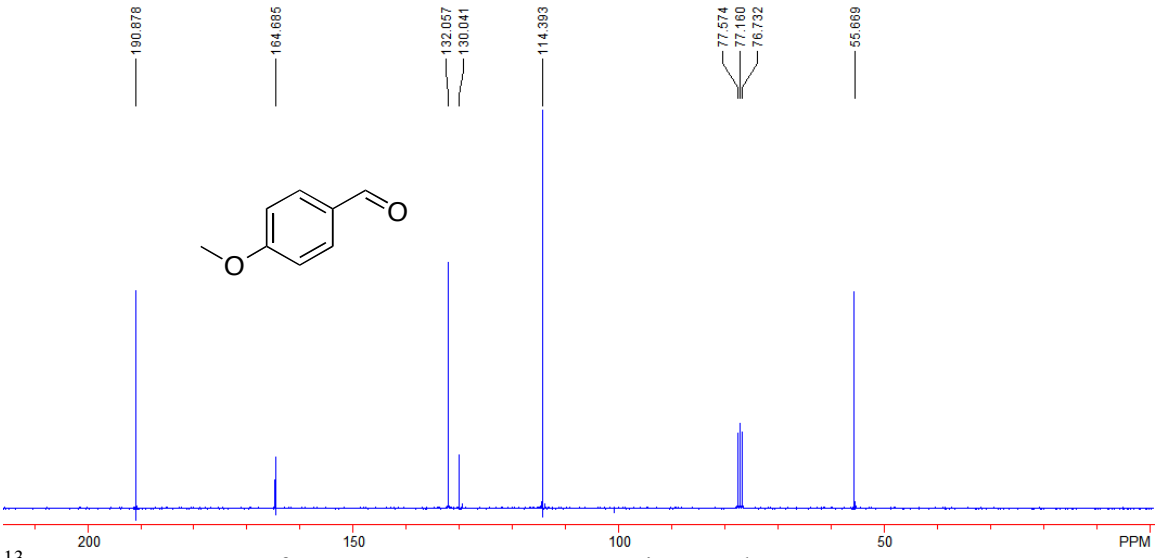


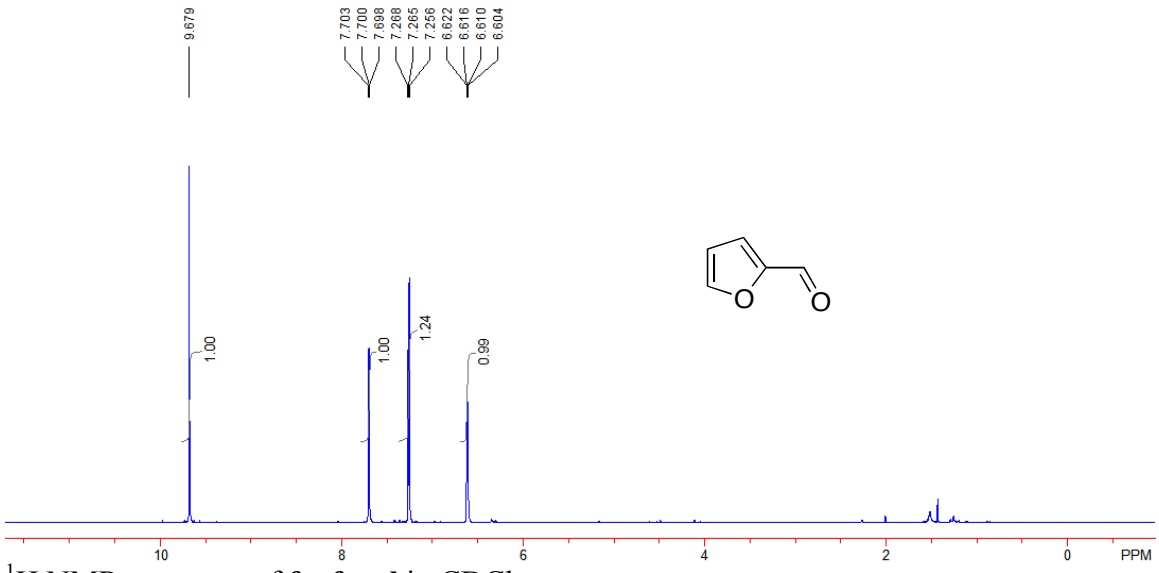
^{1}H NMR spectrum of crude reaction mixture of the oxidation of **5-trimethylsilyl-4-pentynol** in $CDCl_3$.



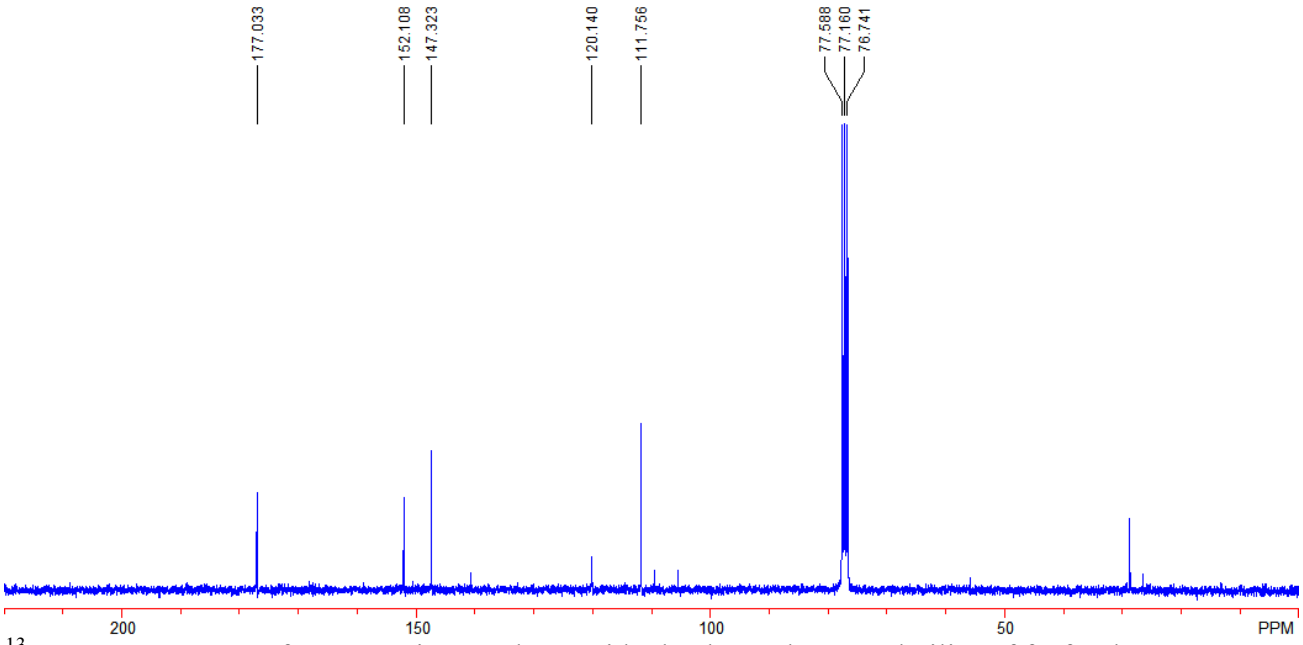
^{1}H NMR spectrum of **4-methoxy-benzaldehyde** in $CDCl_3$.



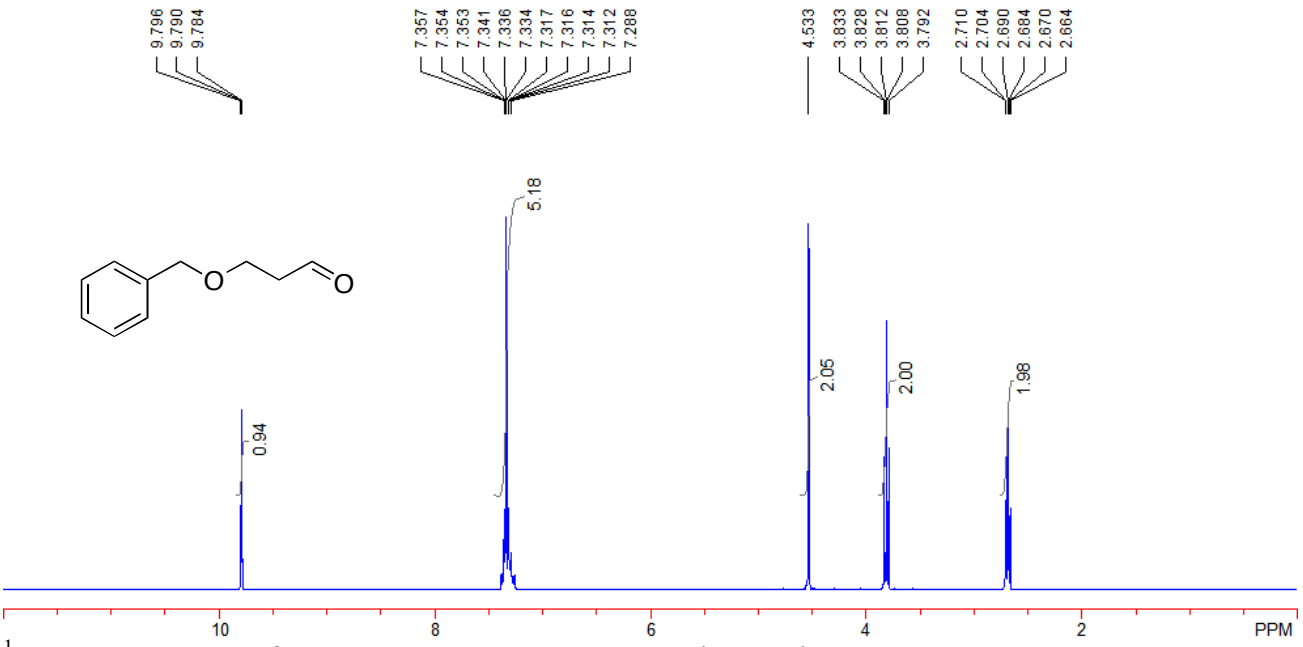
^{13}C NMR spectrum of **4-methoxy-benzaldehyde** in $CDCl_3$.



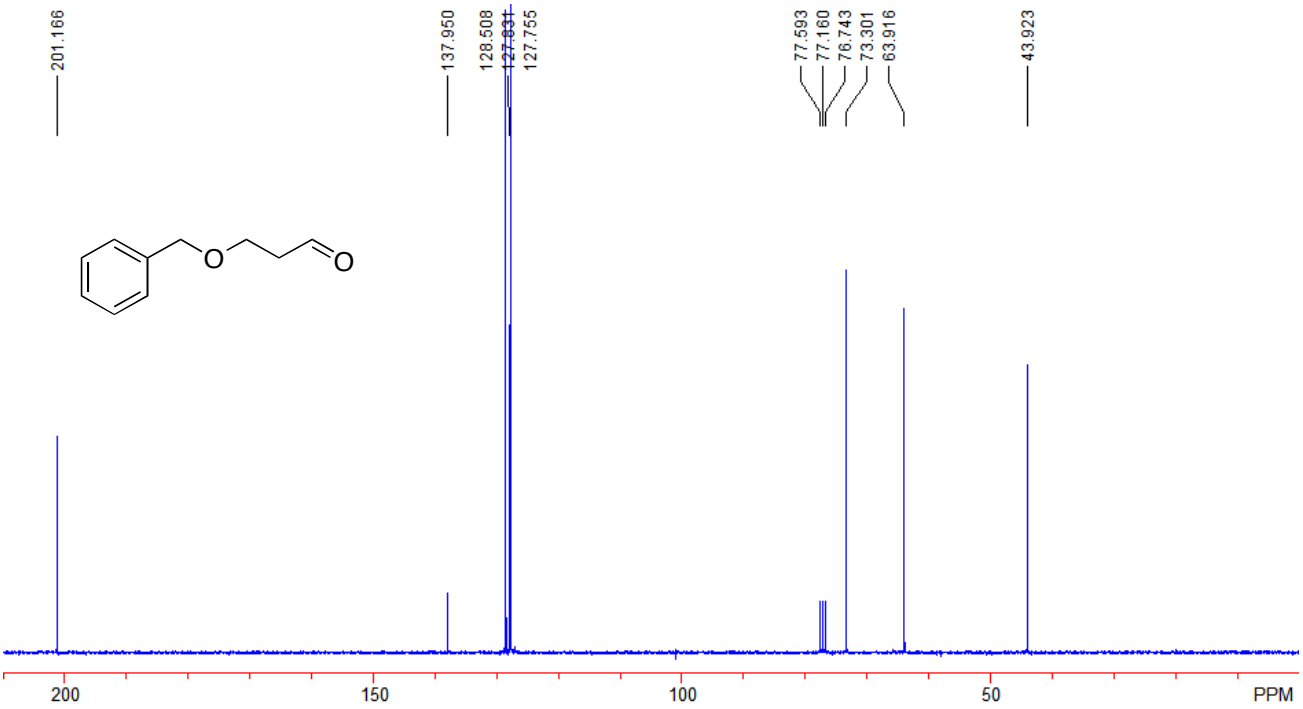
^{1}H NMR spectrum of **furfural** in $CDCl_3$.



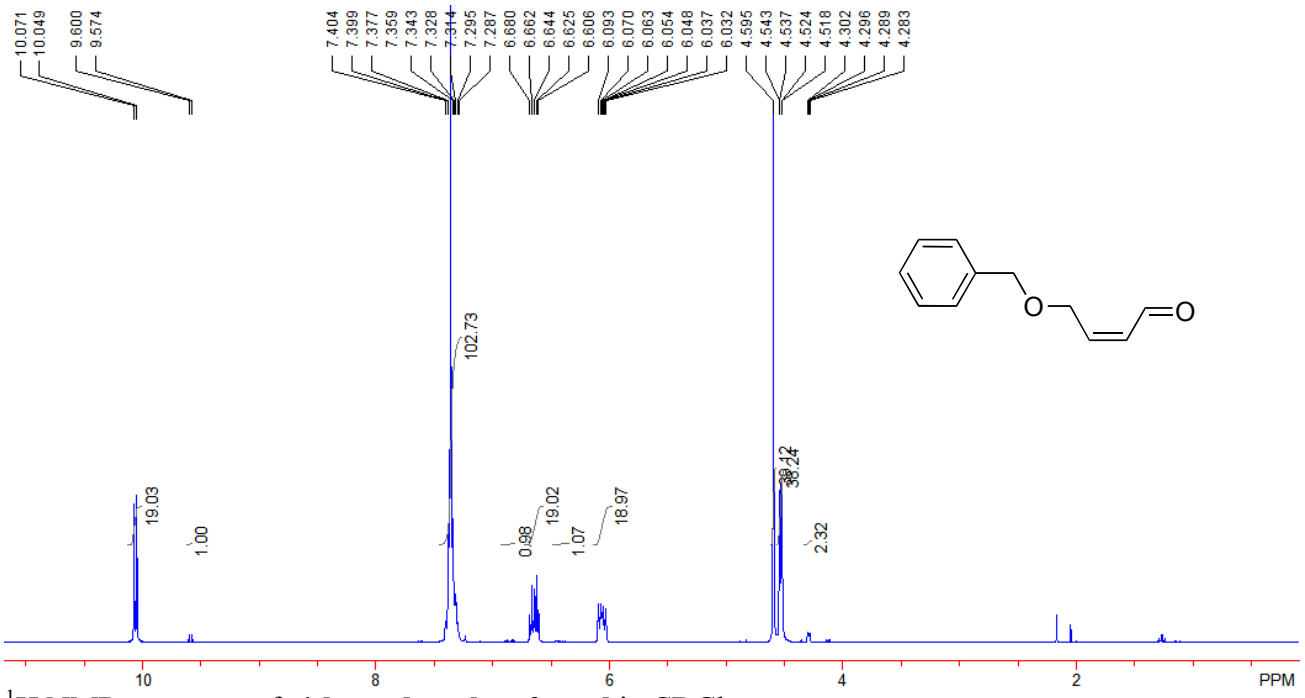
^{13}C NMR spectrum of **furfural** in $CDCl_3$. Residual solvent due to volatility of furfural.



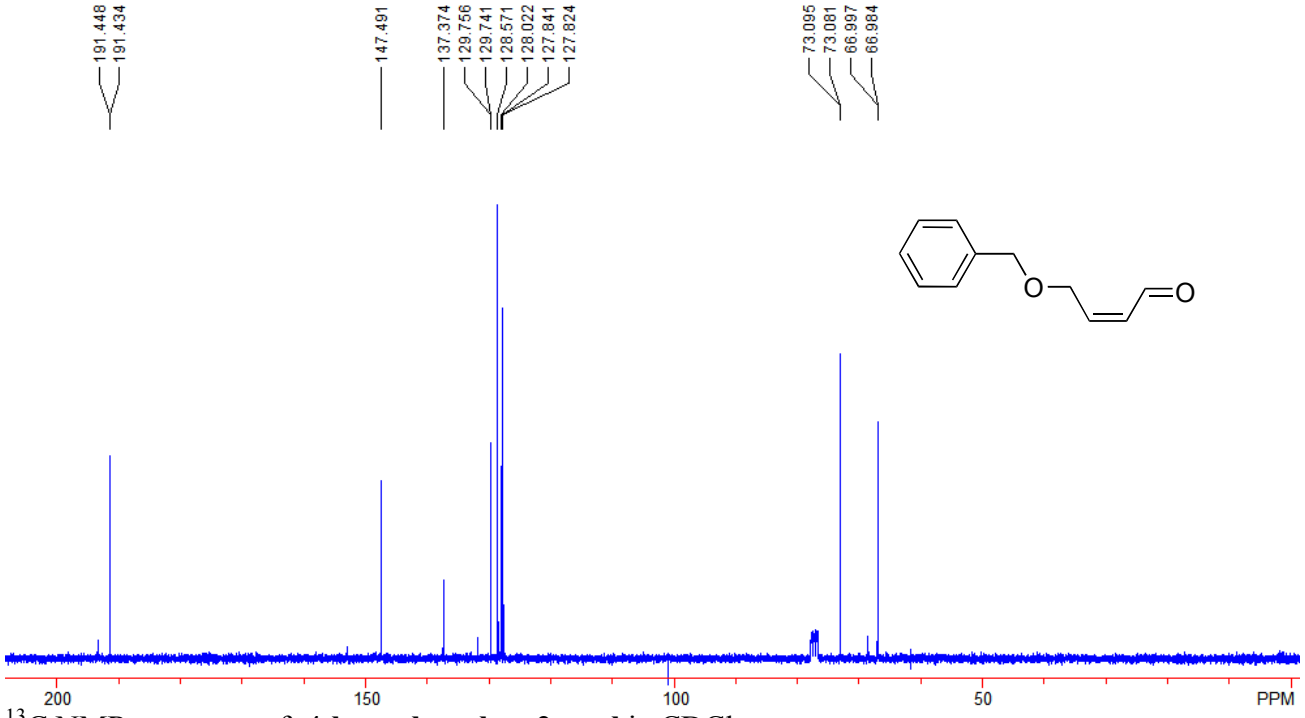
^{1}H NMR spectrum of **3-benzyloxy-propionaldehyde** in $CDCl_3$.



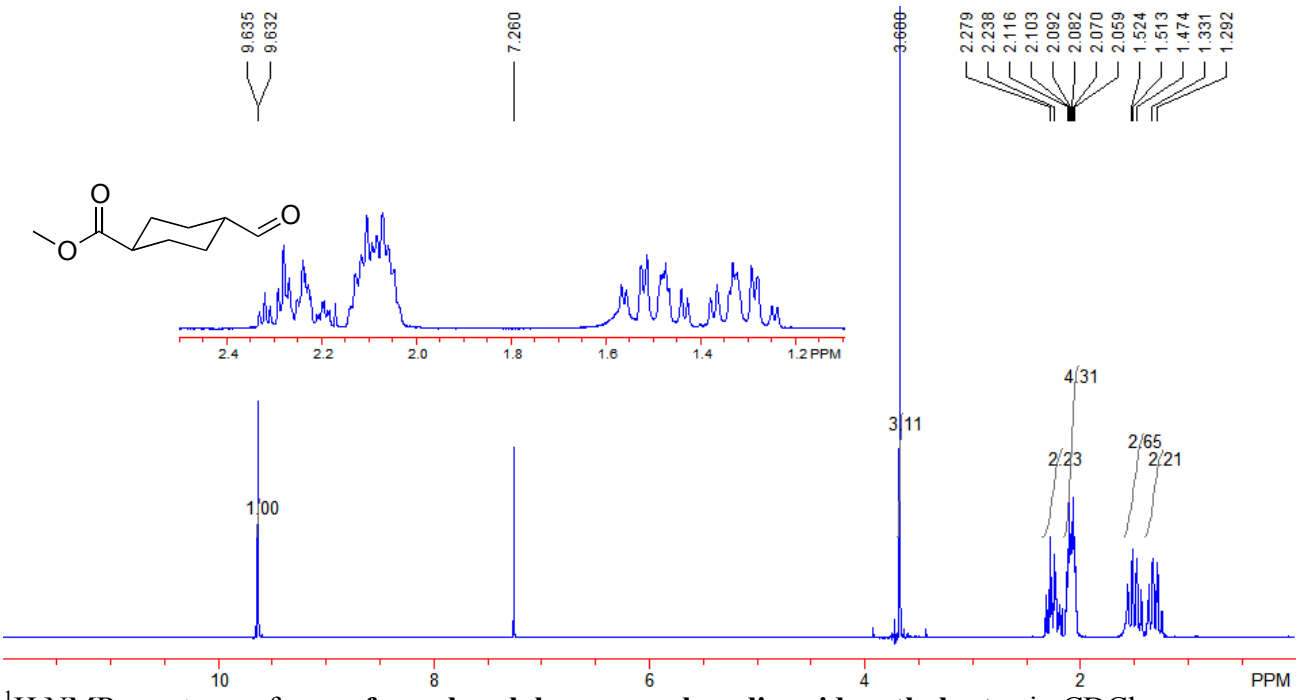
^{13}C NMR spectrum of **3-benzyloxy-propionaldehyde** in $CDCl_3$.



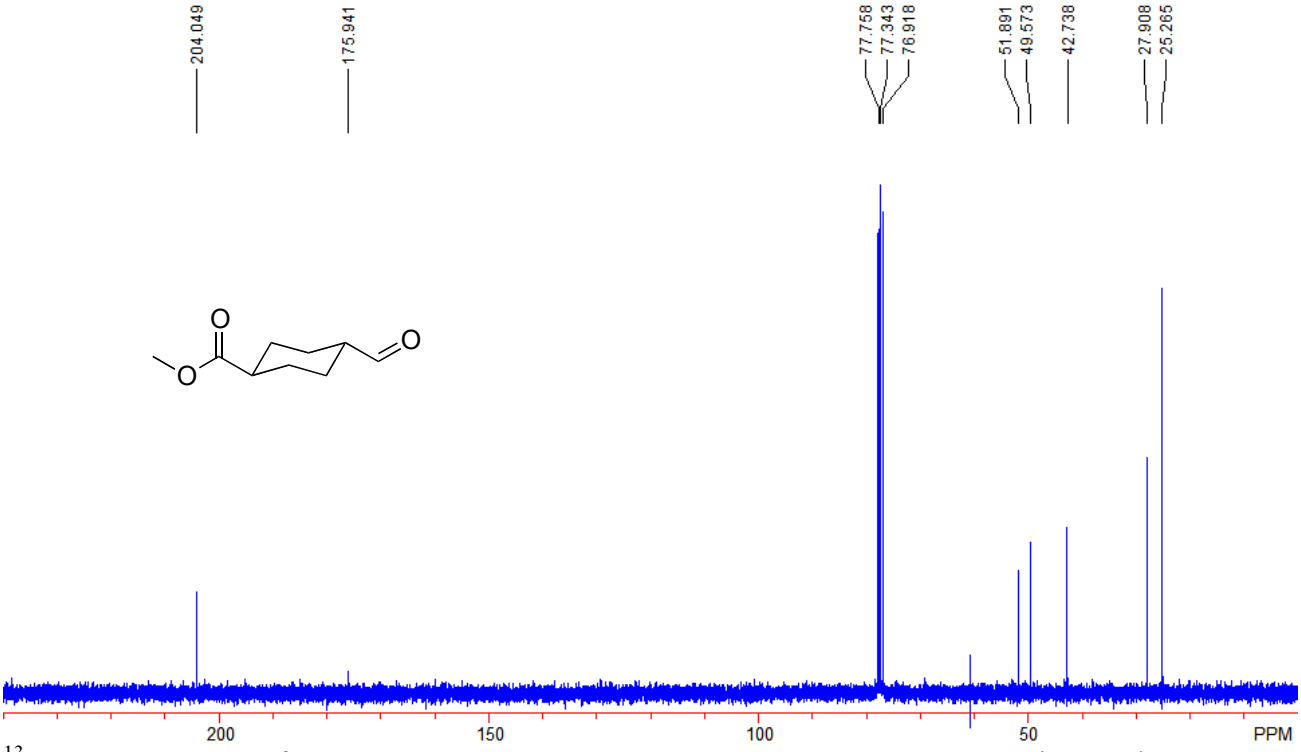
^{1}H NMR spectrum of **4-benzyloxy-but-2-enal** in $CDCl_3$.



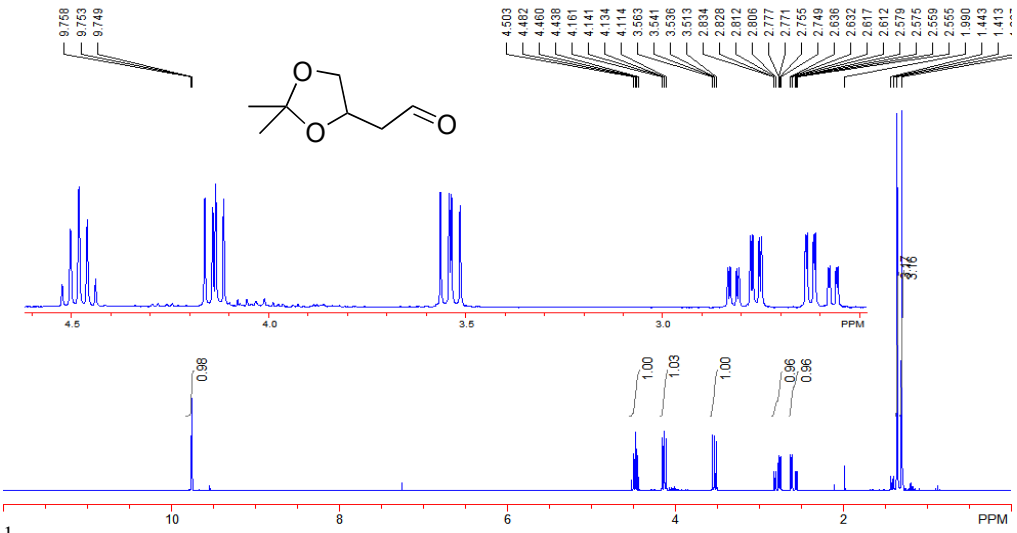
^{13}C NMR spectrum of **4-benzyloxy-but-2-enal** in $CDCl_3$.



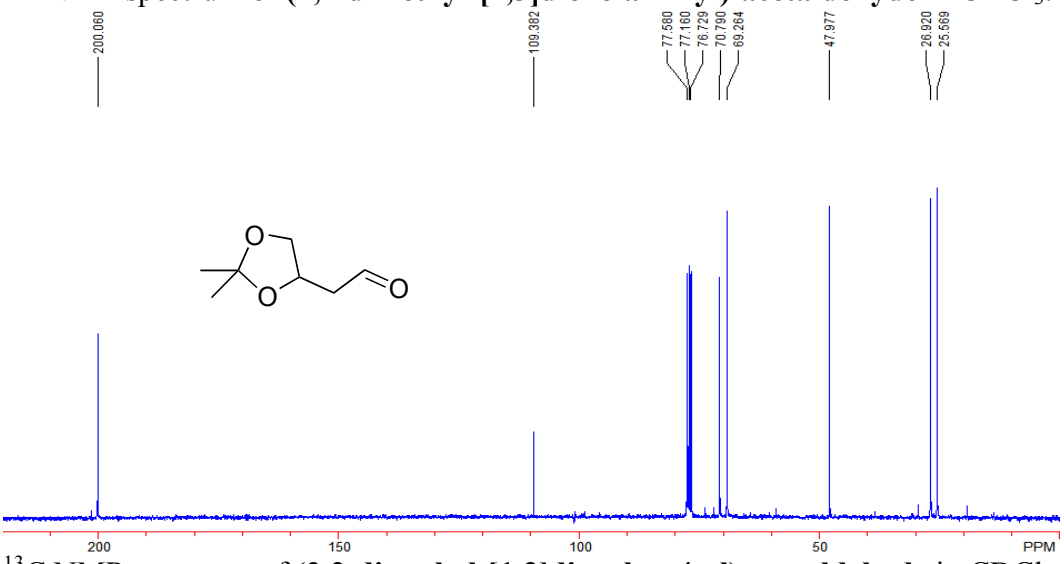
^{1}H NMR spectrum of ***trans*-formyl cyclohexane carboxylic acid methyl ester** in $CDCl_3$.



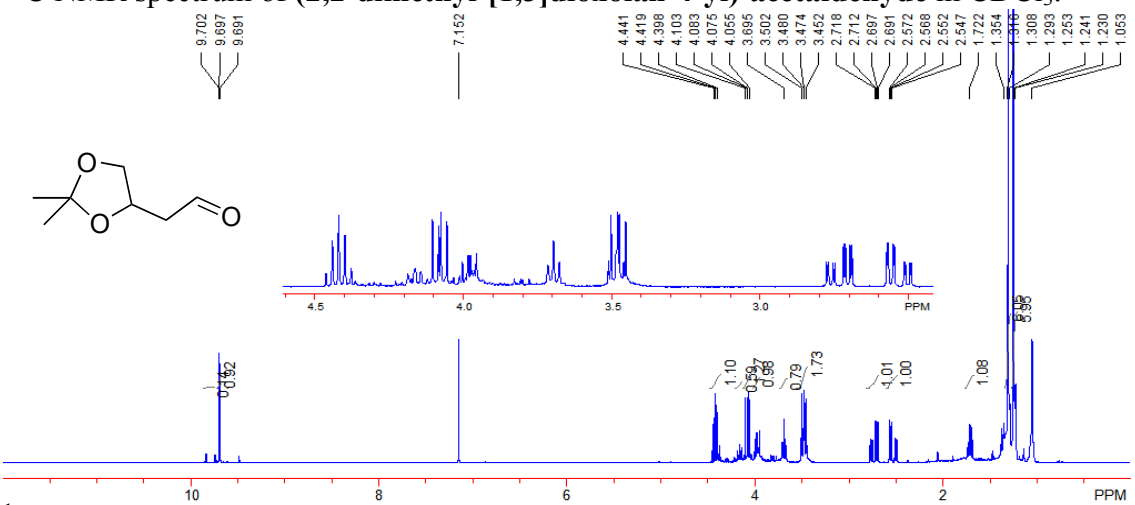
^{13}C NMR spectrum of ***trans*-formyl cyclohexane carboxylic acid methyl ester** in $CDCl_3$.



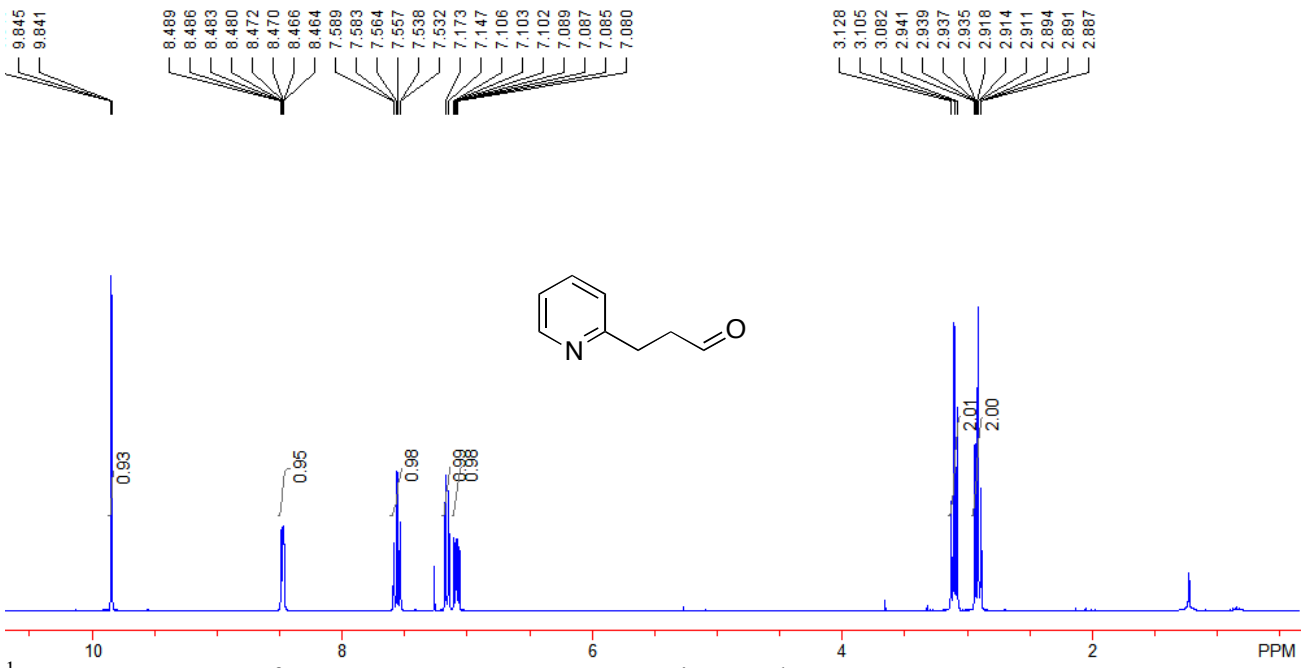
^{1}H NMR spectrum of **(2,2-dimethyl-[1,3]dioxolan-4-yl)-acetaldehyde** in $CDCl_3$.



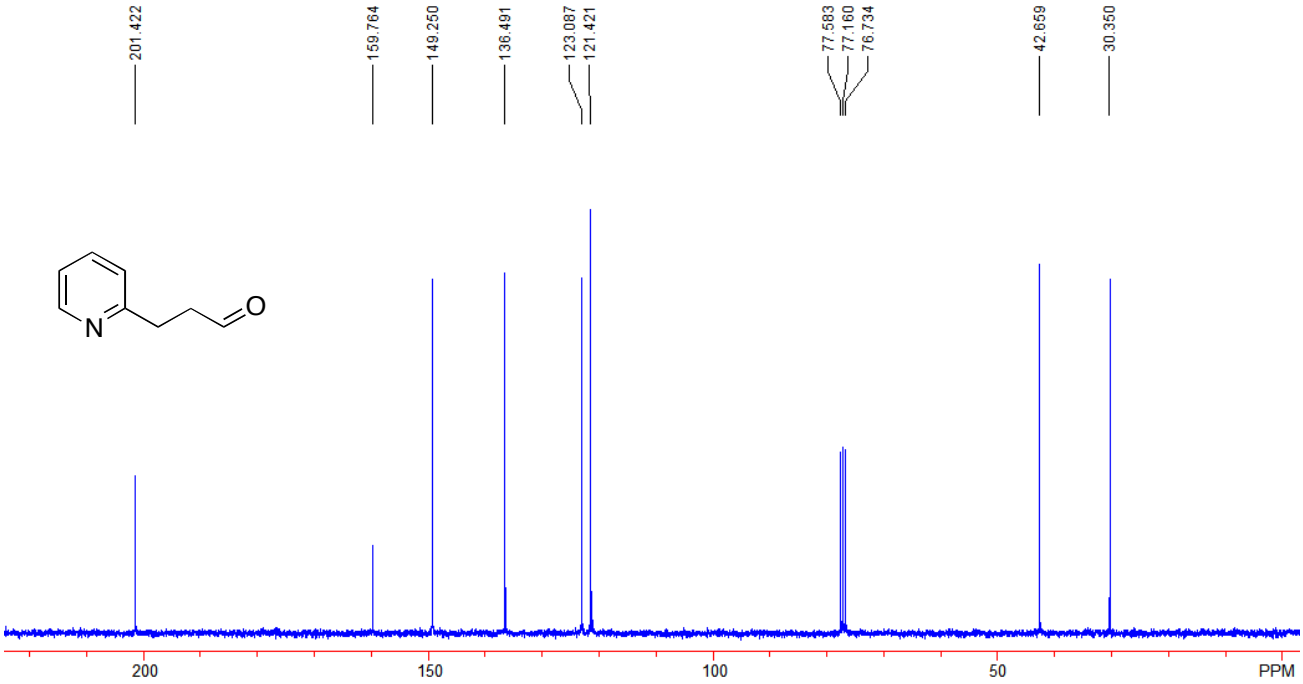
^{13}C NMR spectrum of **(2,2-dimethyl-[1,3]dioxolan-4-yl)-acetaldehyde** in $CDCl_3$.



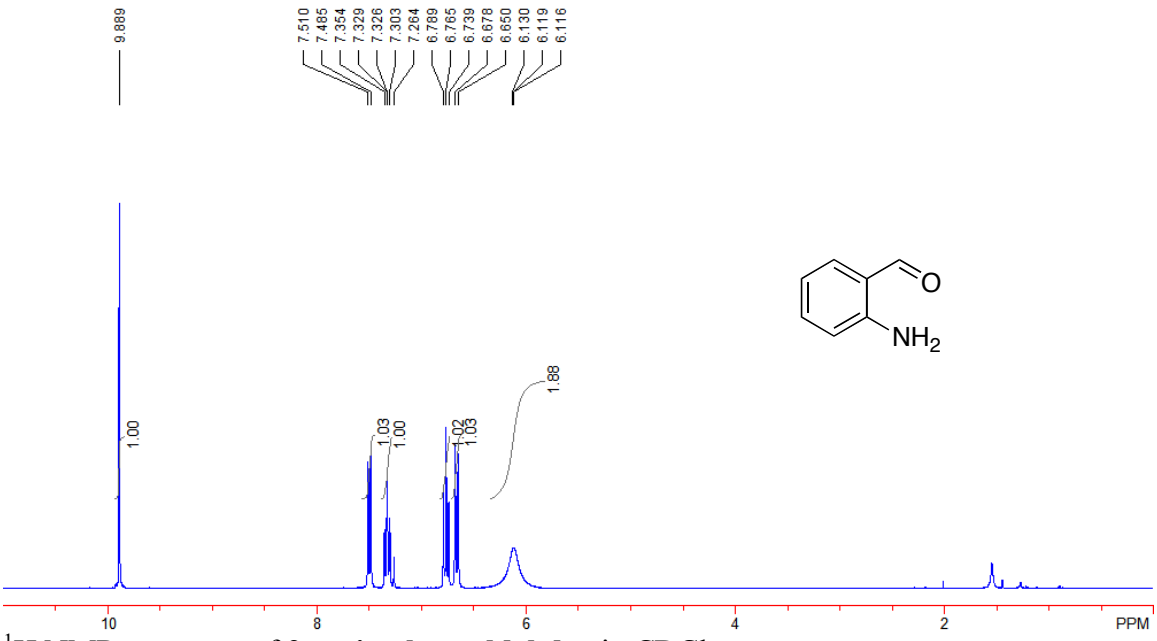
^{1}H NMR spectrum of crude reaction mixture **(2,2-dimethyl-[1,3]dioxolan-4-yl)-acetaldehyde** in $CDCl_3$.



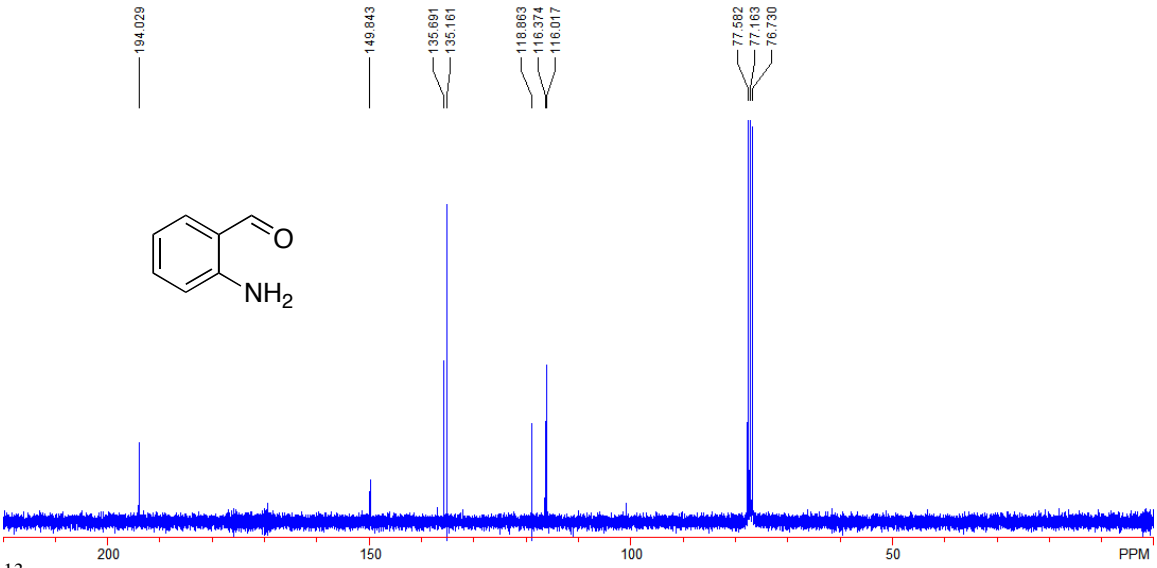
^{1}H NMR spectrum of **3-pyridine-propionaldehyde** in $CDCl_3$.



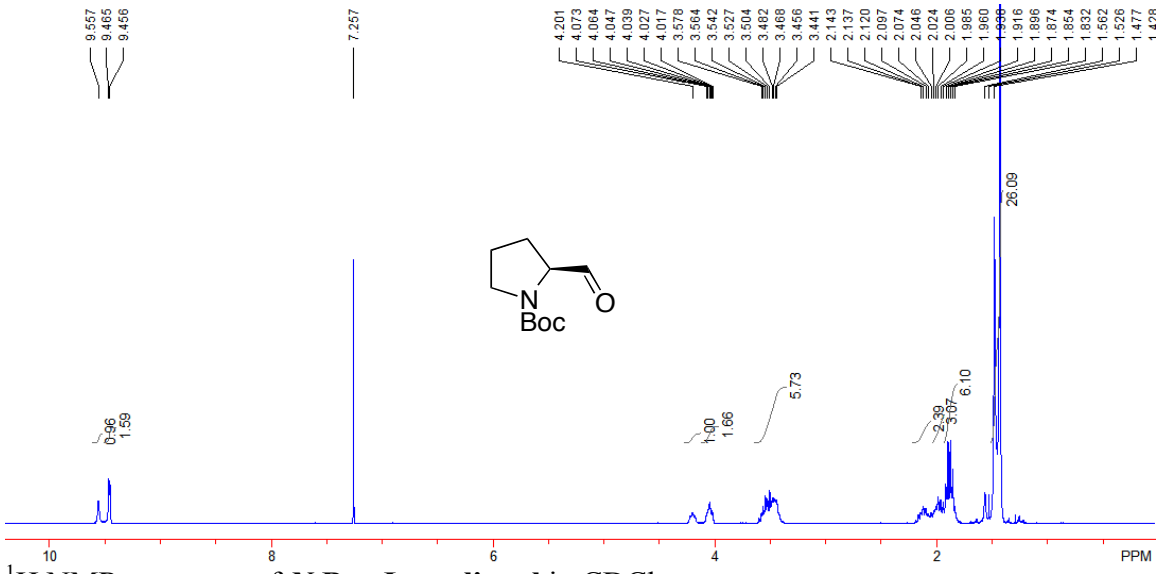
^{13}C NMR spectrum of **3-pyridine-propionaldehyde**in $CDCl_3$.



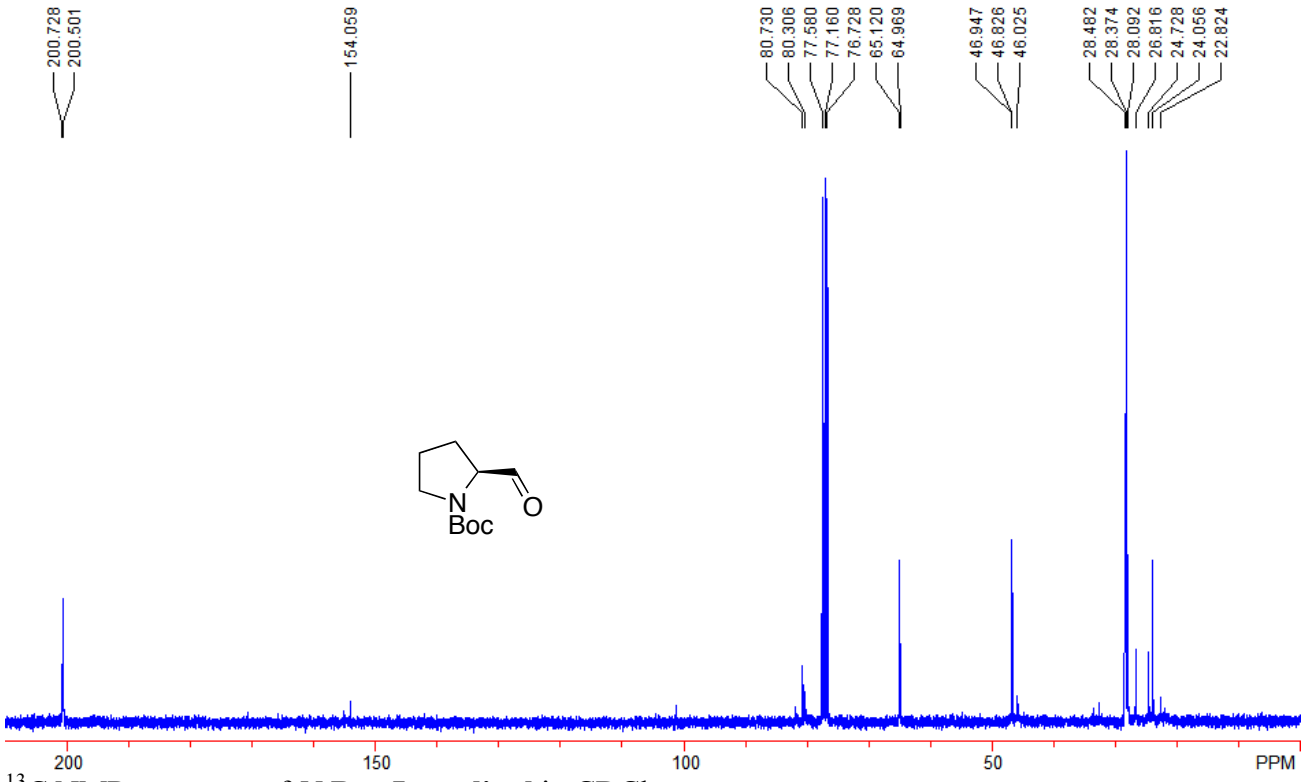
^{1}H NMR spectrum of **2-amino benzaldehdye** in $CDCl_3$.



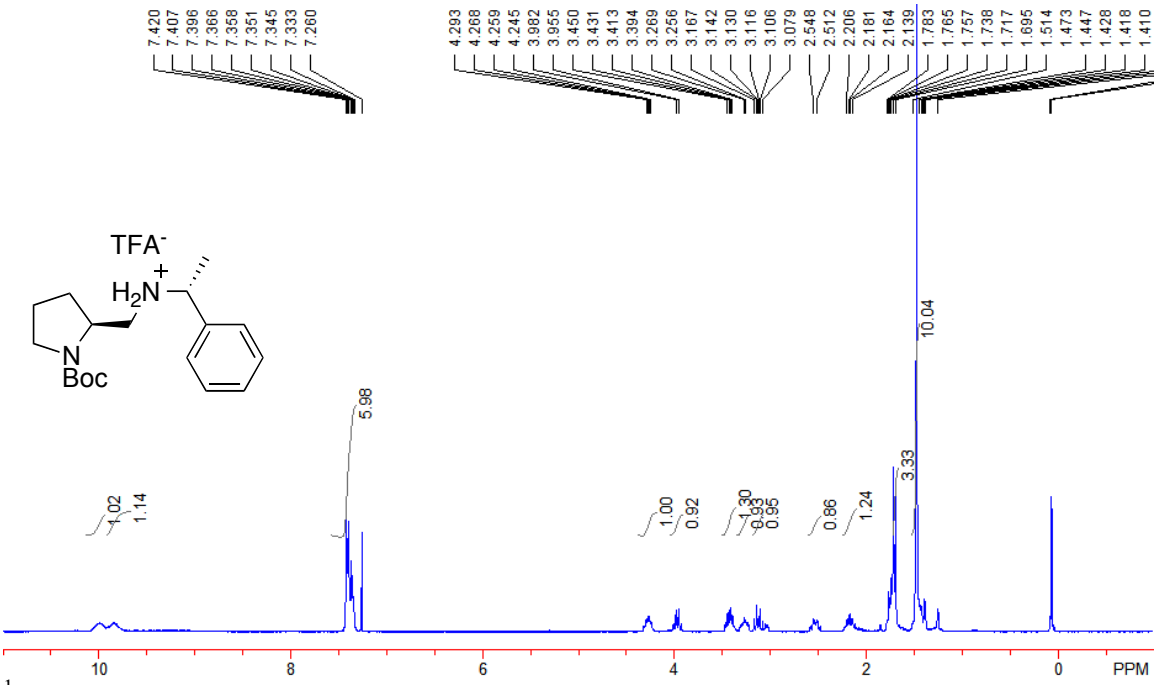
^{13}C NMR spectrum of **2-amino benzaldehyde** in $CDCl_3$.



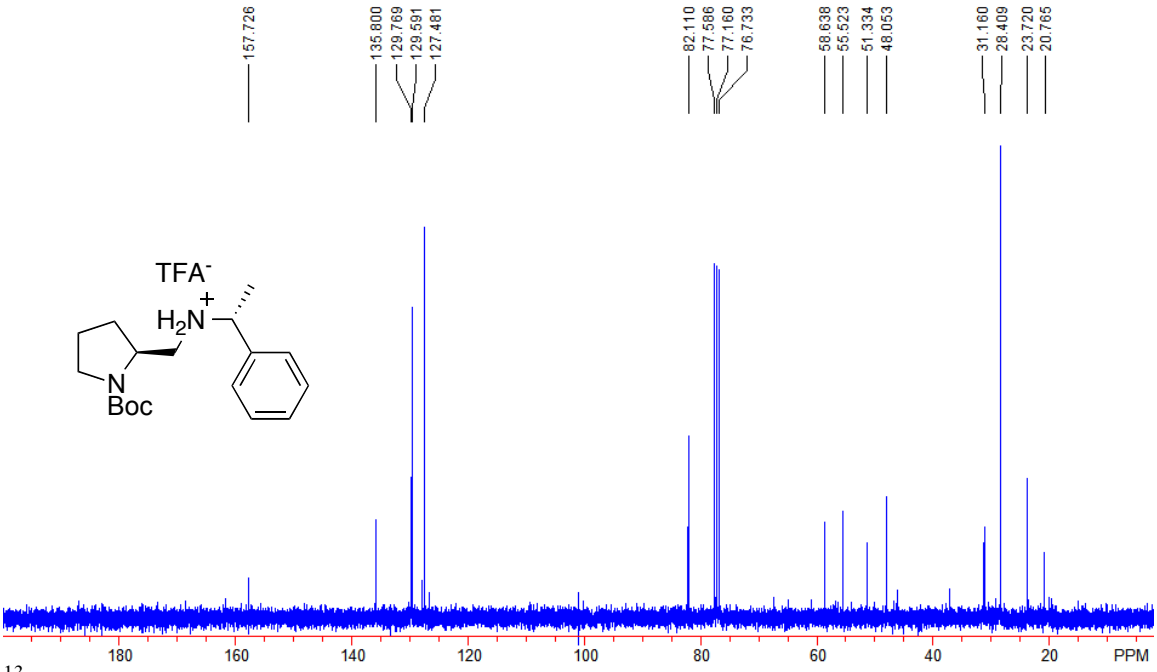
^{1}H NMR spectrum of ***N*-Boc-L-prolional** in $CDCl_3$.



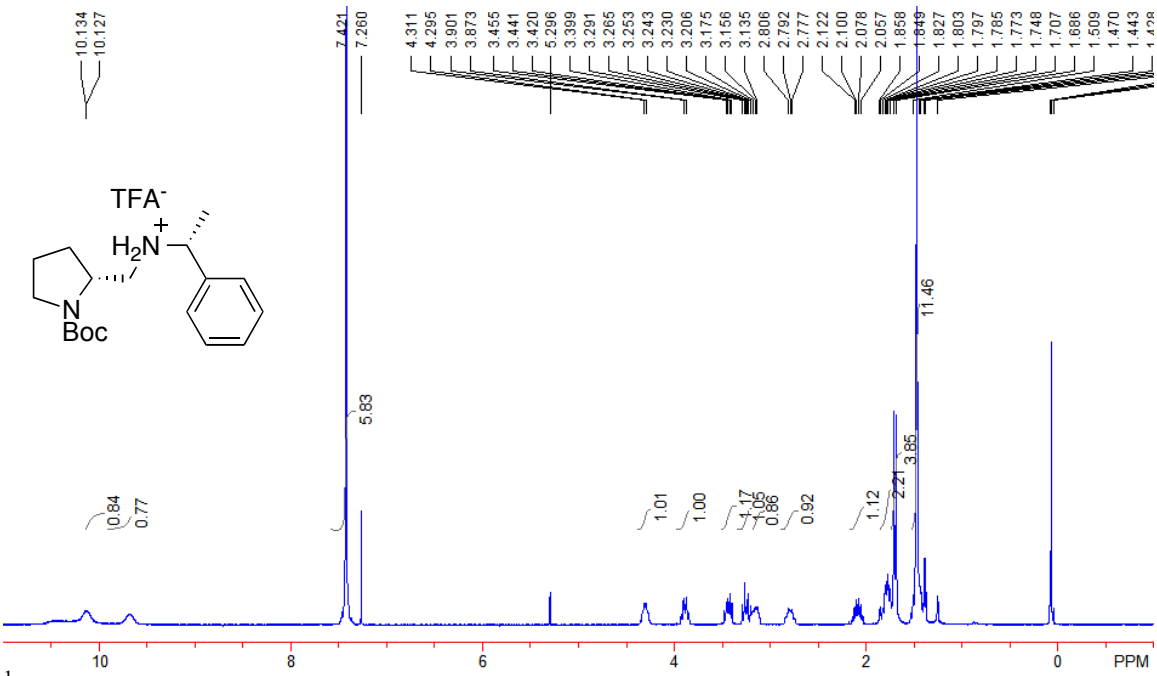
^{13}C NMR spectrum of ***N*-Boc-L-prolinal** in $CDCl_3$.



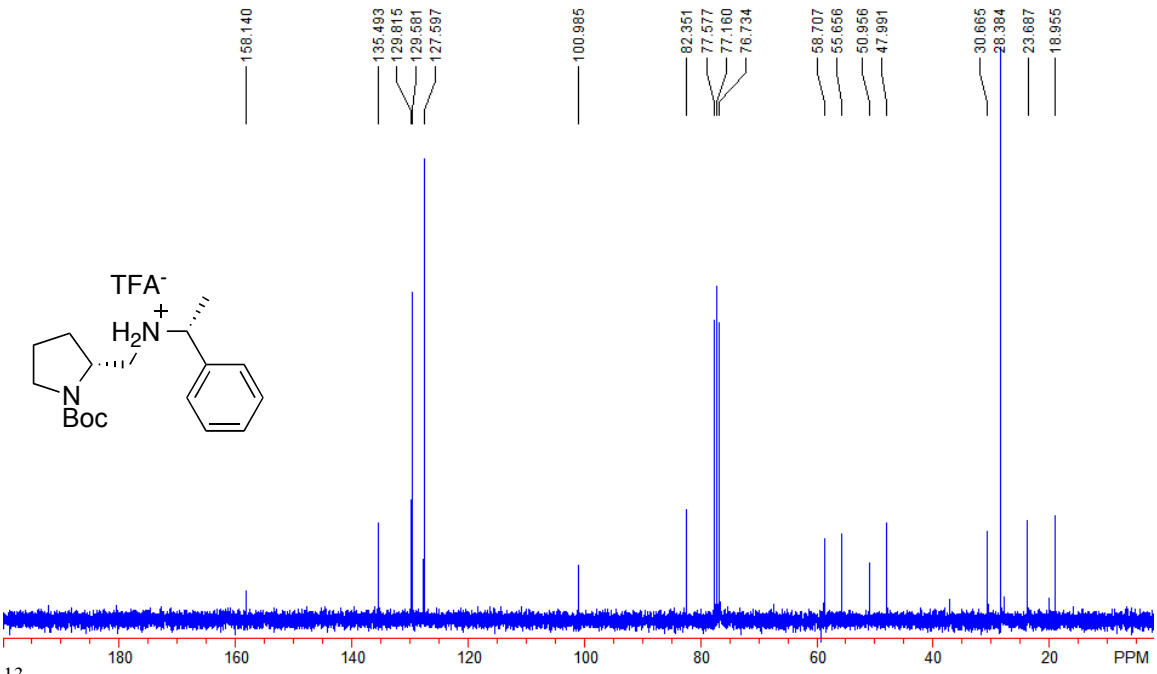
^{1}H NMR spectrum of **2-[(R-1-[phenyl-ethylammoinum)-methyl]-*N*-Boc-L-pyrrolidine trifluoroacetate** in $CDCl_3$.



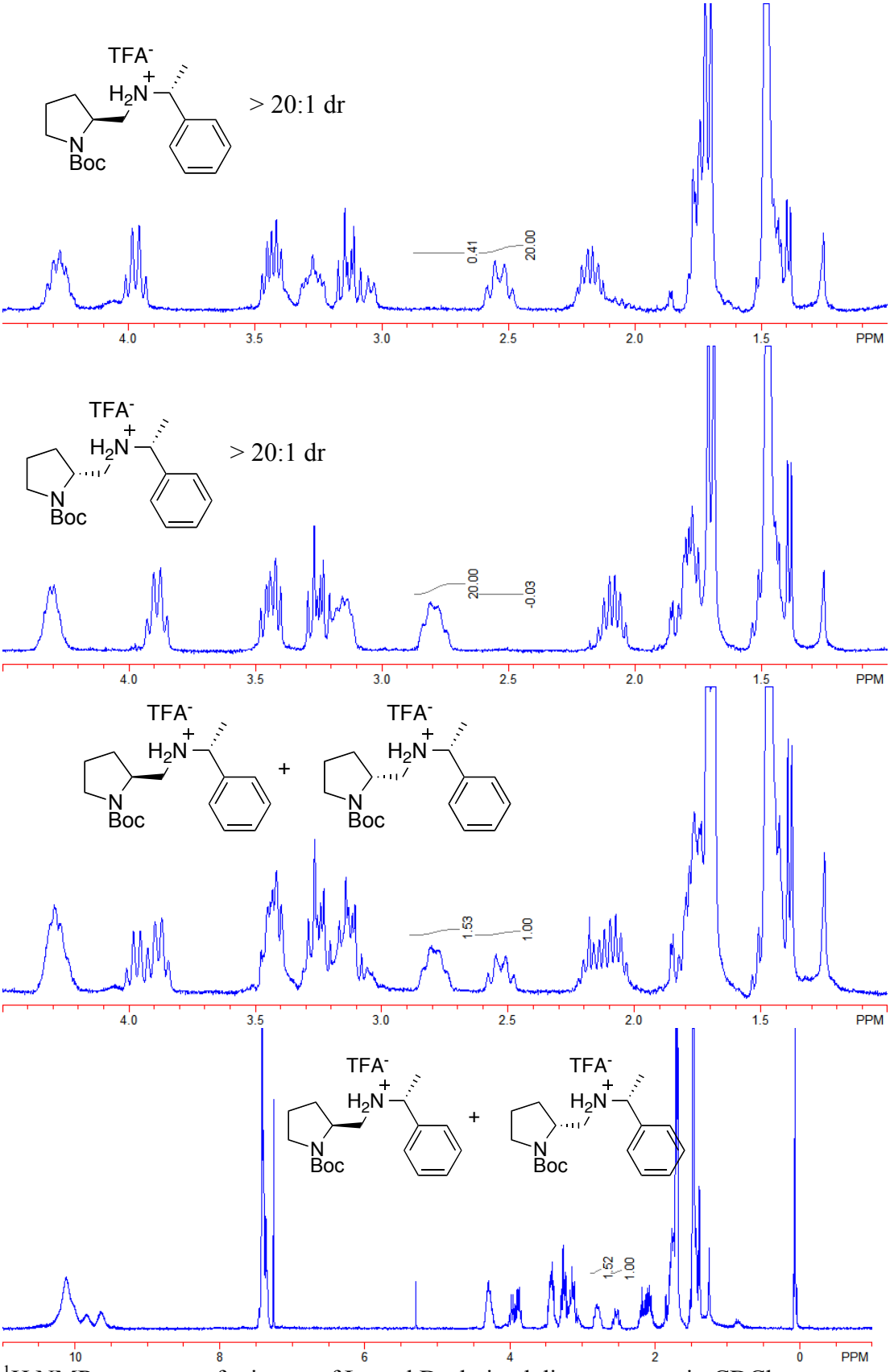
^{13}C NMR spectrum of **2-[(R-1-[phenyl-ethylammoinum)-methyl]-*N*-Boc-L-pyrrolidine trifluoroacetate** in $CDCl_3$.



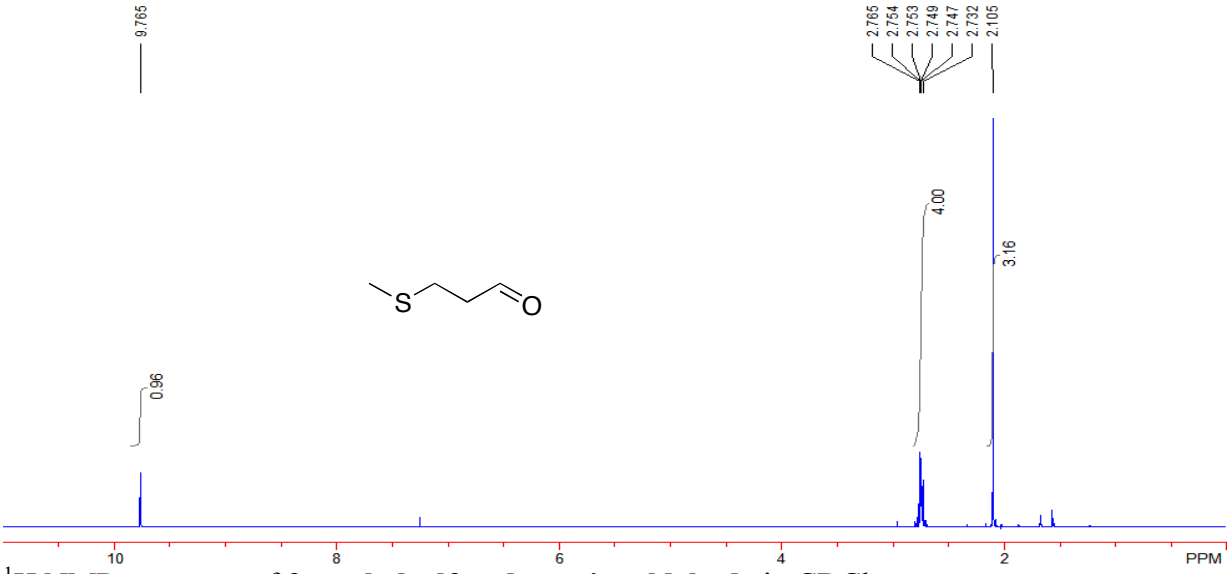
^{1}H NMR spectrum of **2-[(R-1-[phenyl-ethylammoinum)-methyl]-*N*-Boc-D-pyrrolidine trifluoroacetate** in $CDCl_3$.



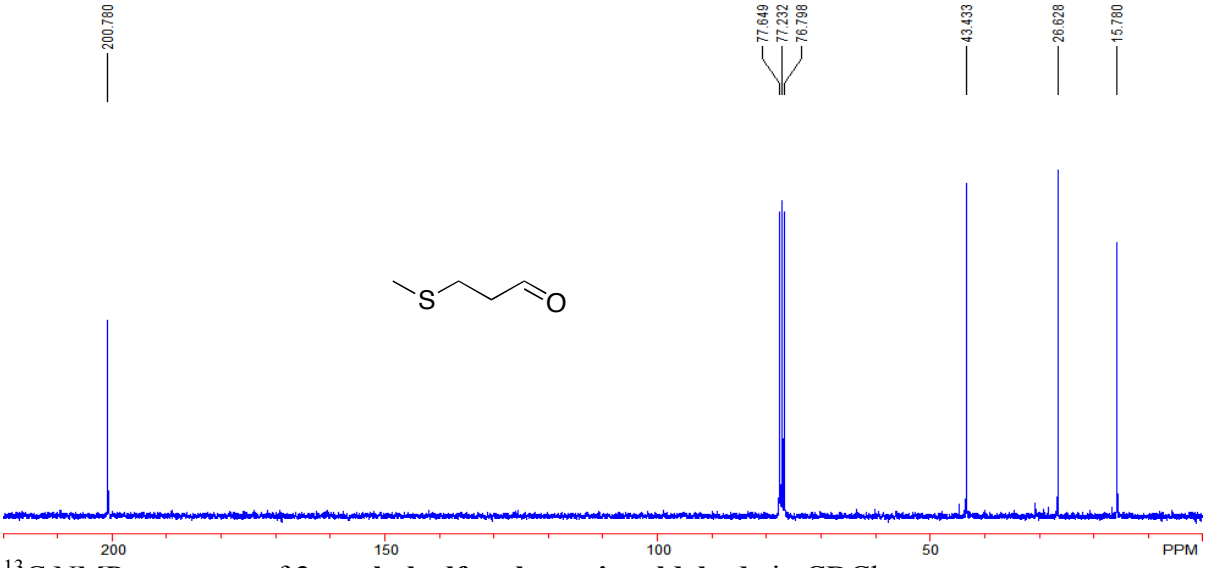
^{13}C NMR spectrum of **2-[(R-1-[phenyl-ethylammoinum)-methyl]-*N*-Boc-D-pyrrolidine trifluoroacetate** in $CDCl_3$.



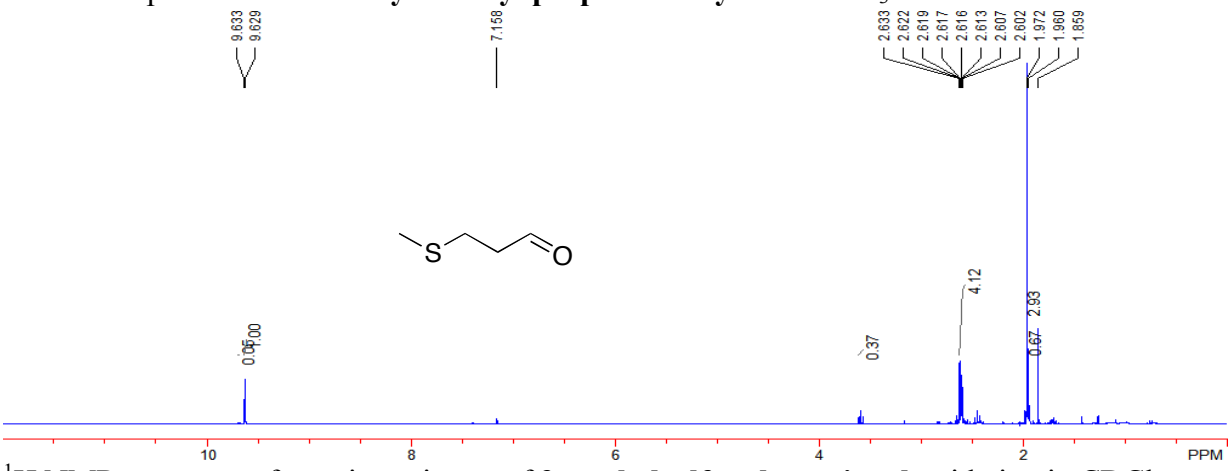
^{1}H NMR spectrum of mixture of L- and D- derived diastereomers in $CDCl_3$.



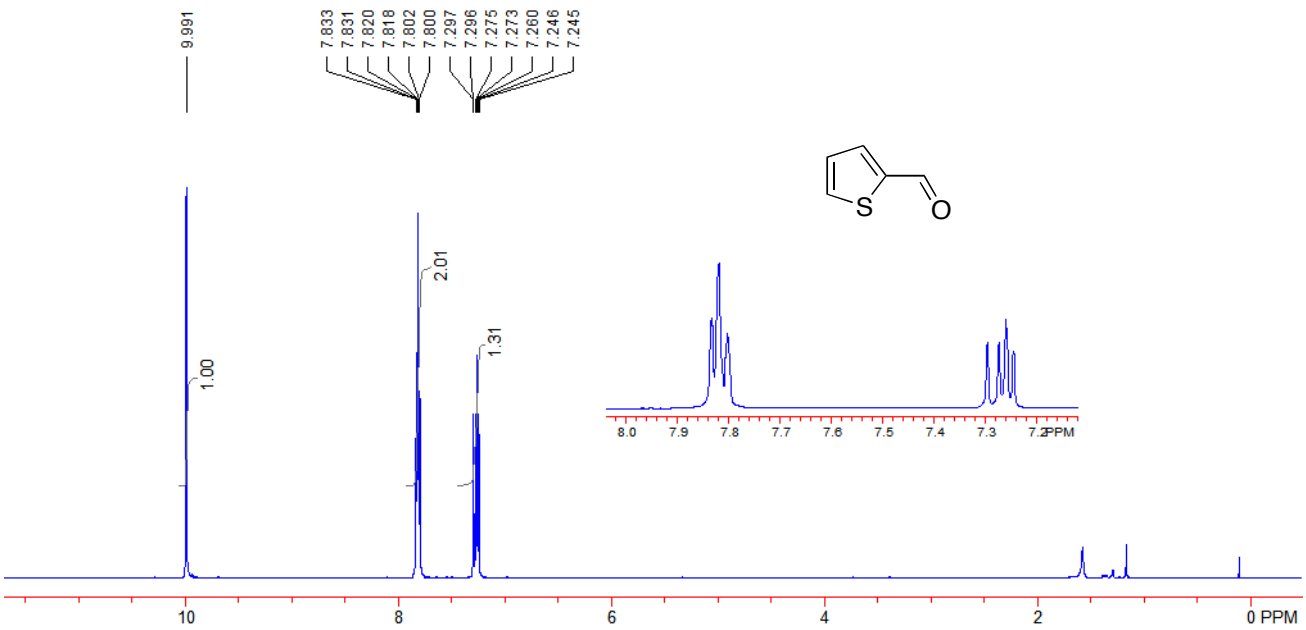
^{1}H NMR spectrum of **3-methylsulfanyl propionaldehyde** in $CDCl_3$.



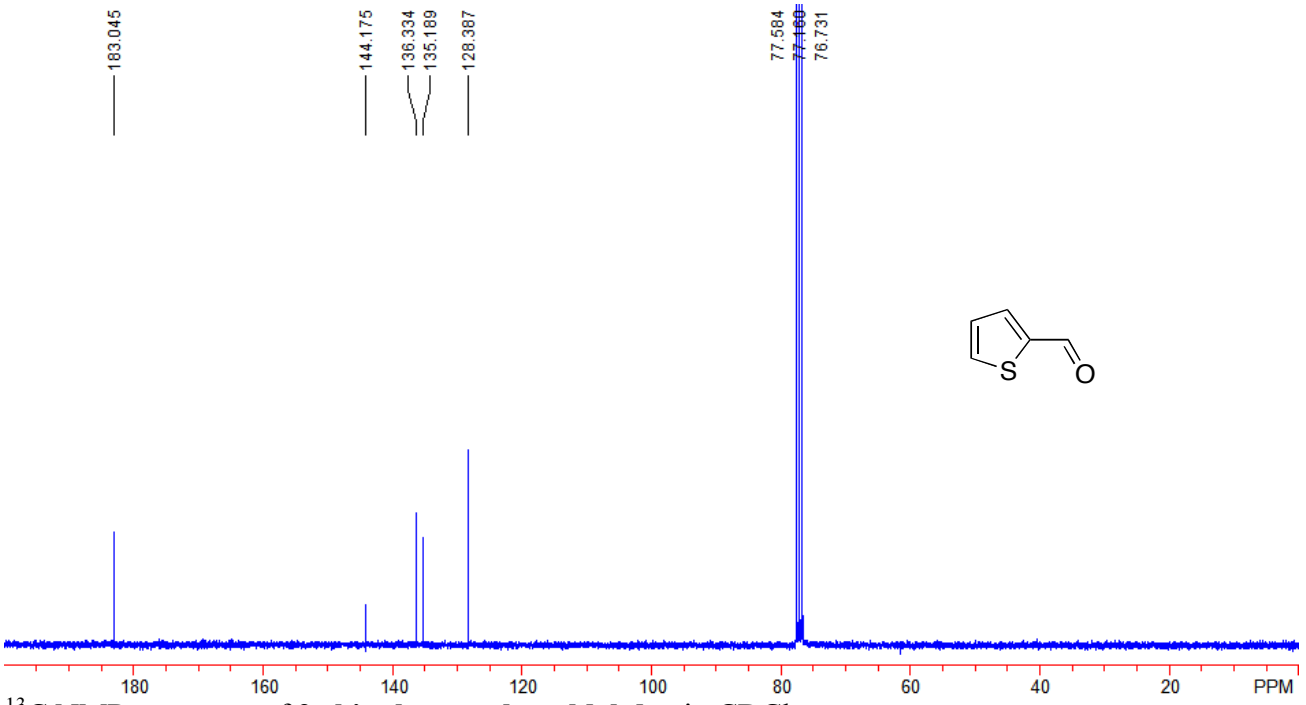
^{13}C NMR spectrum of **3-methylsulfanyl propionaldehyde** in $CDCl_3$.



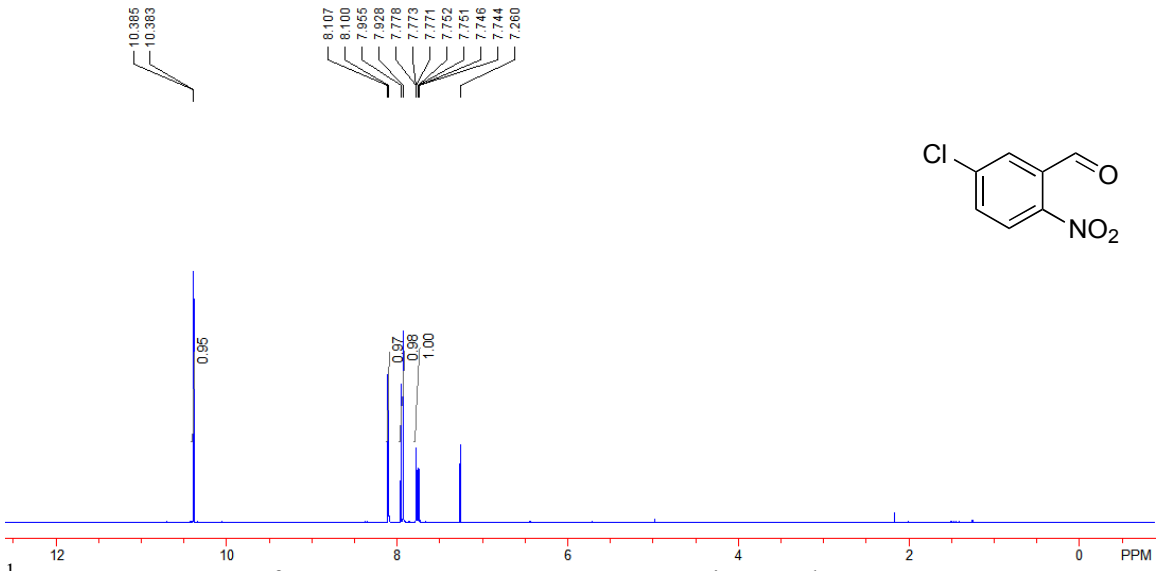
^{1}H NMR spectrum of reaction mixture of **3-methylsulfanyl propionol** oxidation in $CDCl_3$.



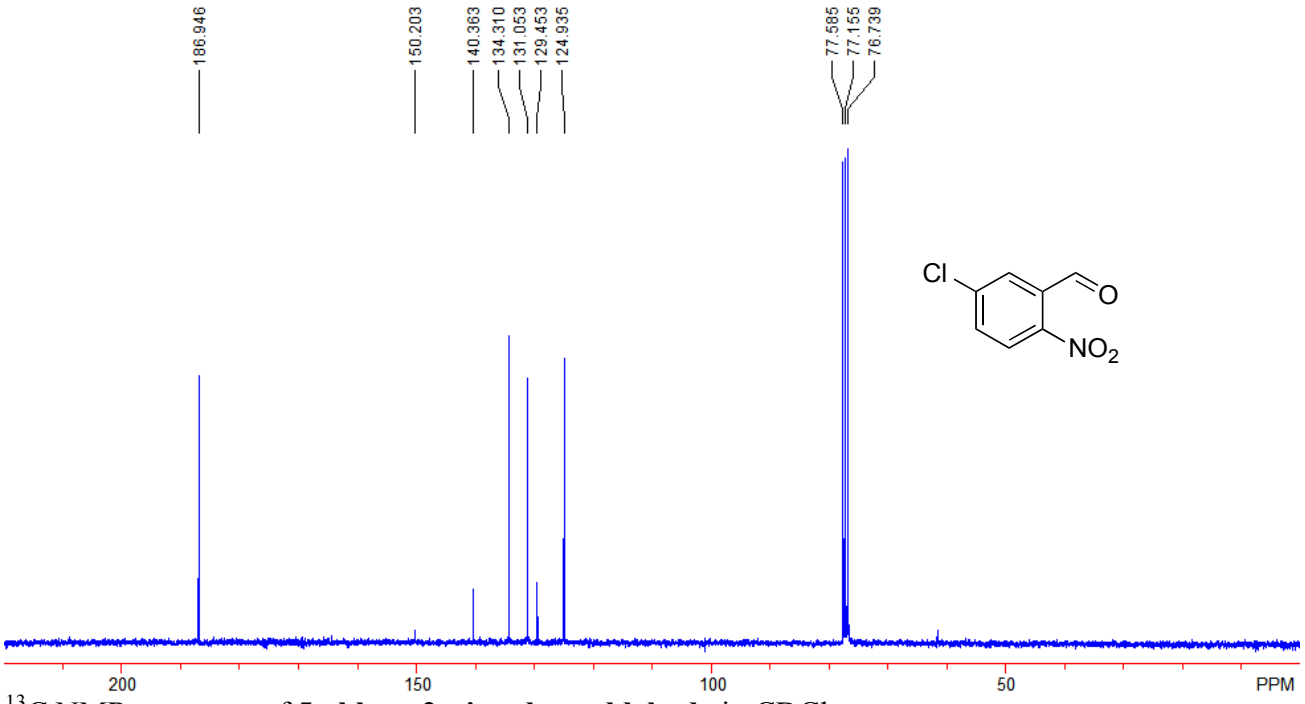
^{1}H NMR spectrum of **2-thiophenecarboxaldehyde** in $CDCl_3$.



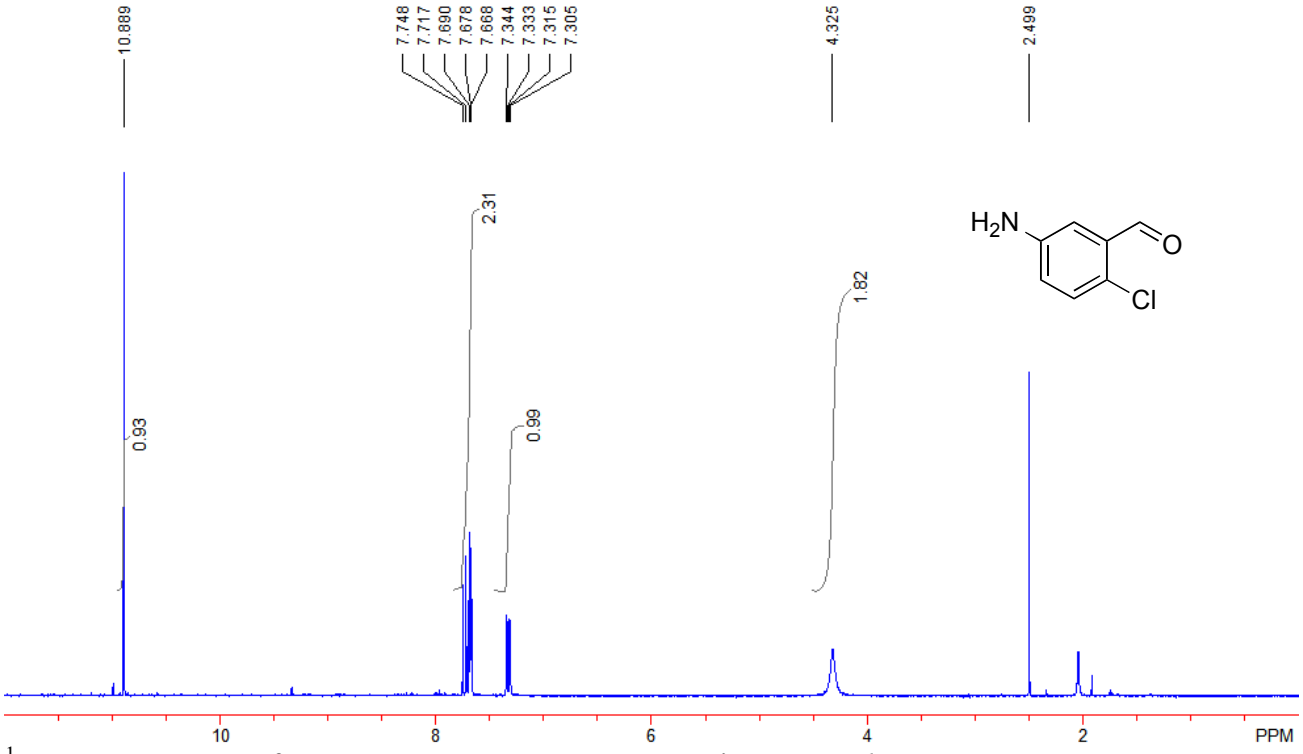
^{13}C NMR spectrum of **2-thiophenecarboxaldehdye** in $CDCl_3$.



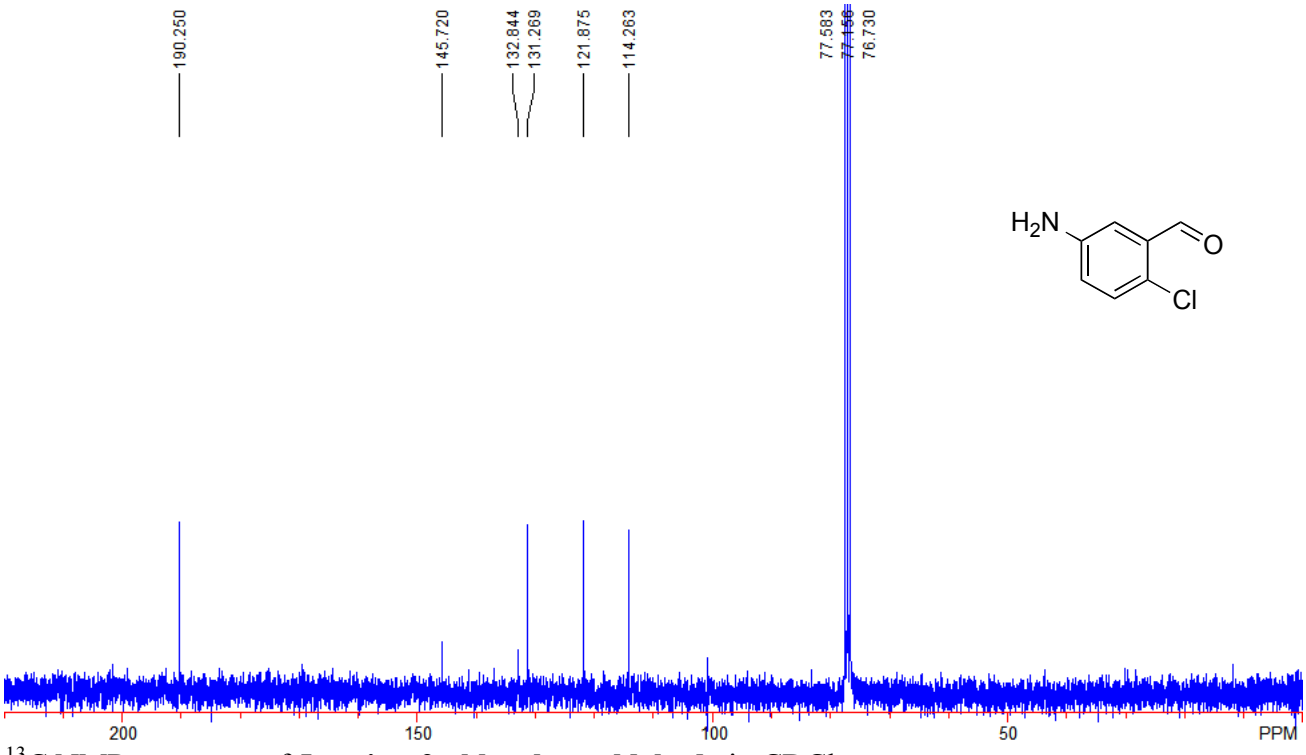
^{1}H NMR spectrum of **5-chloro-2-nitro-benzaldehyde** in $CDCl_3$.



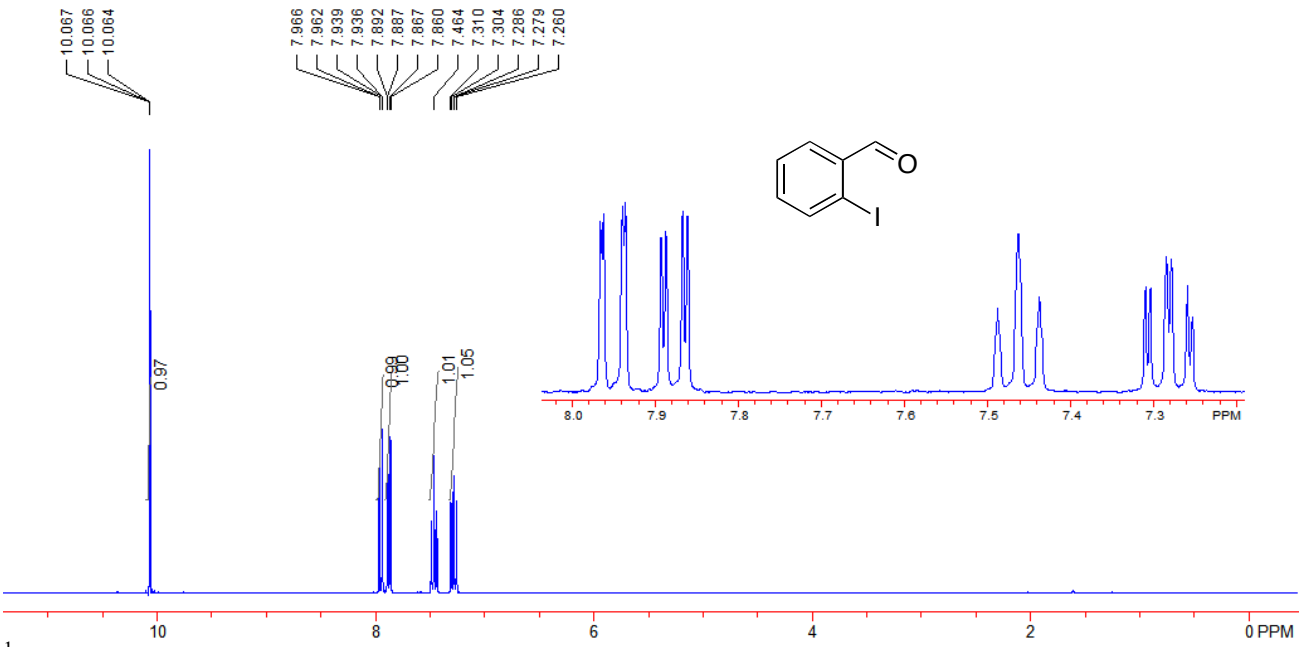
^{13}C NMR spectrum of **5-chloro-2-nitro-benzaldehyde** in $CDCl_3$.



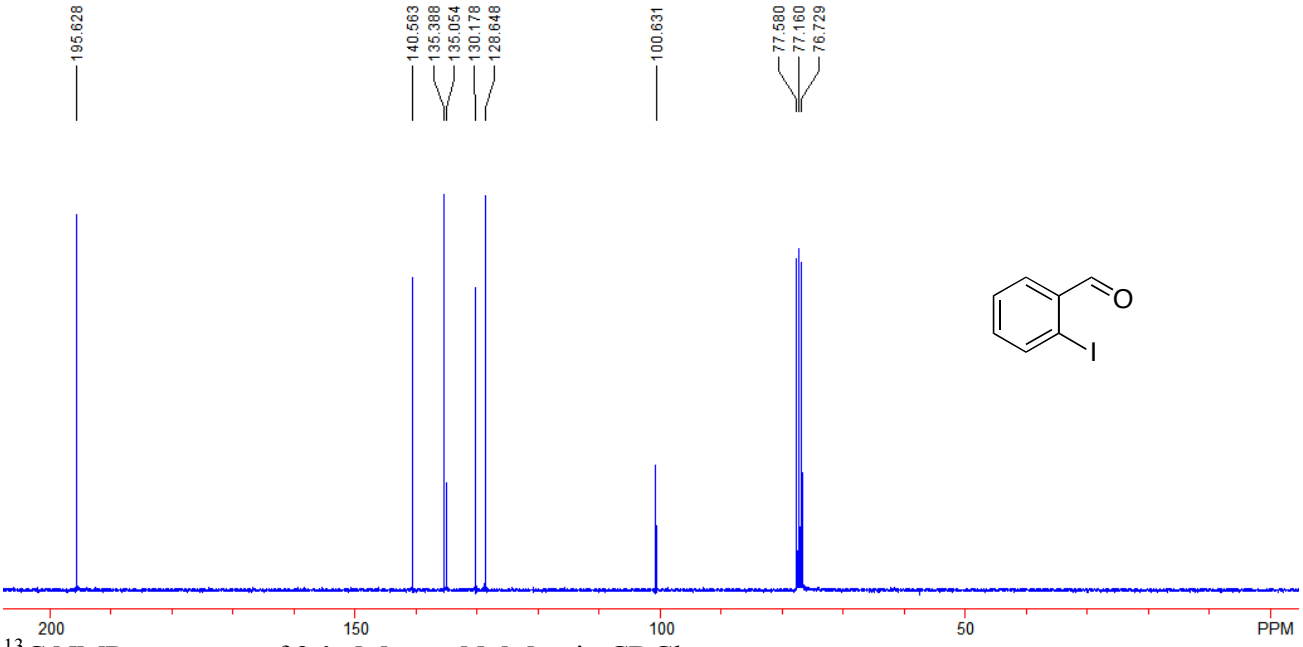
^{1}H NMR spectrum of **5-amino-2-chlorobenzaldehyde** in DMSO-d_6.



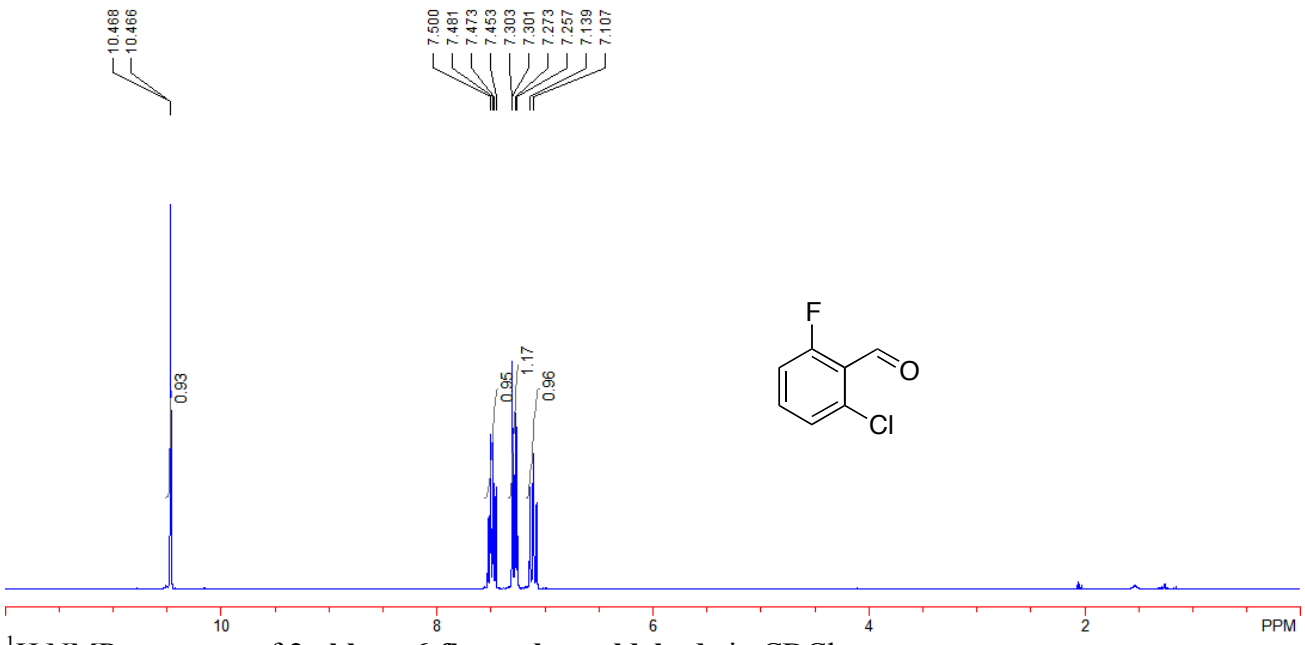
^{13}C NMR spectrum of **5-amino-2-chlorobenzaldehyde** in $CDCl_3$.



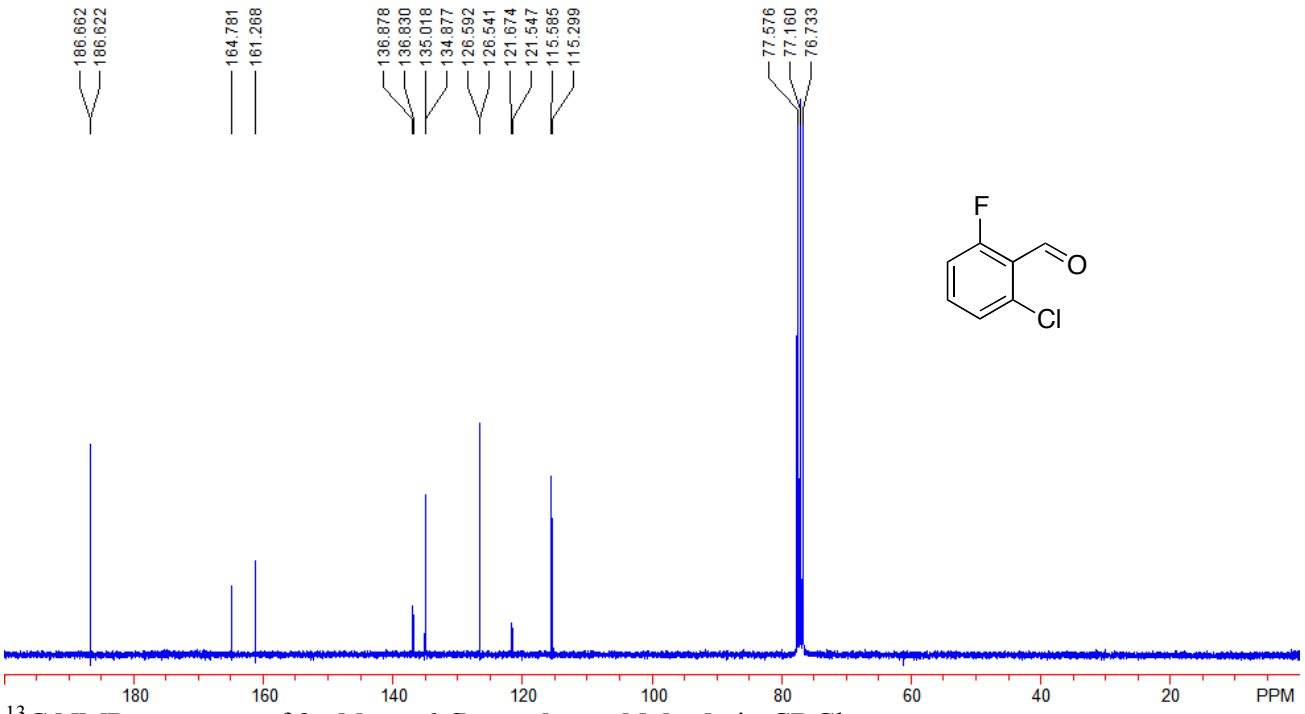
^{1}H NMR spectrum of **2-iodobenzaldehyde** in $CDCl_3$.



^{13}C NMR spectrum of **2-iodobenzaldehdye** in $CDCl_3$.

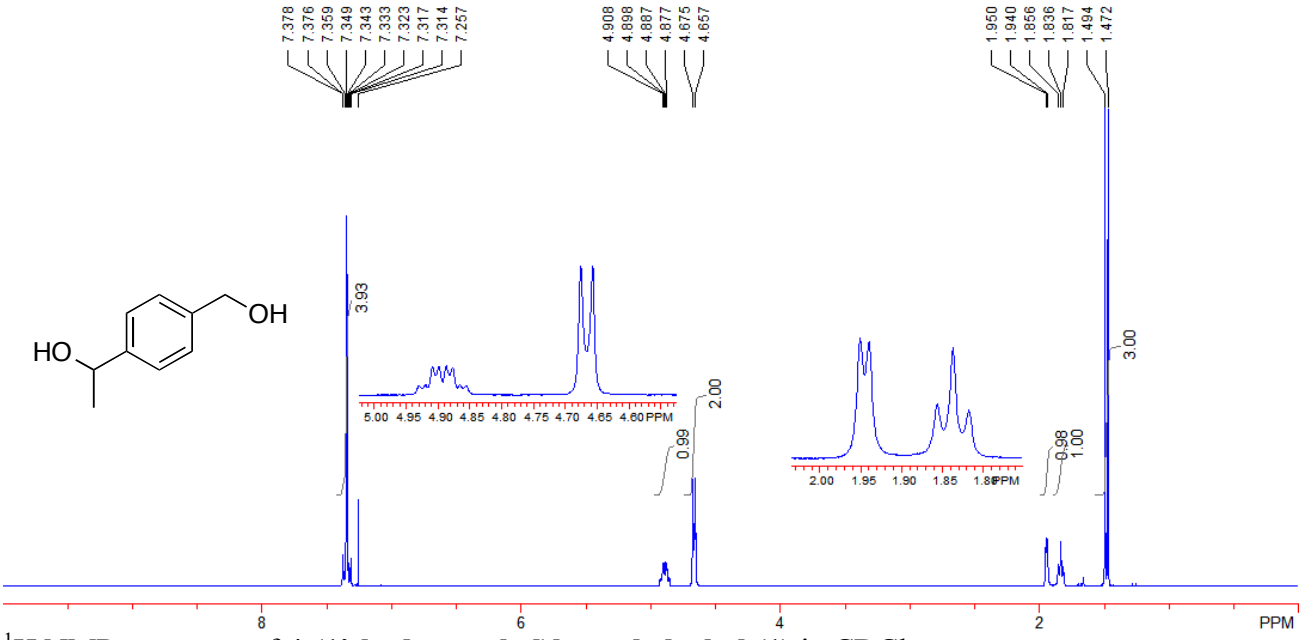


^{1}H NMR spectrum of **2-chloro-6-fluoro-benzaldehyde** in $CDCl_3$.

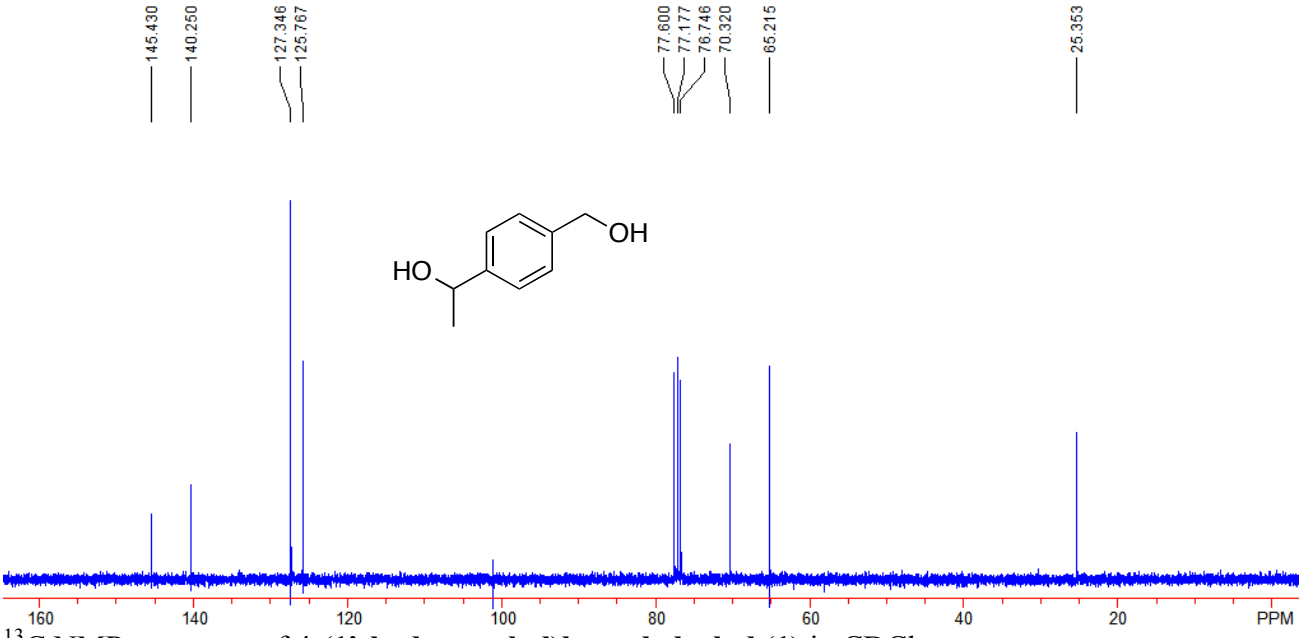


^{13}C NMR spectrum of **2-chloro-6-fluoro-benzaldehyde** in $CDCl_3$.

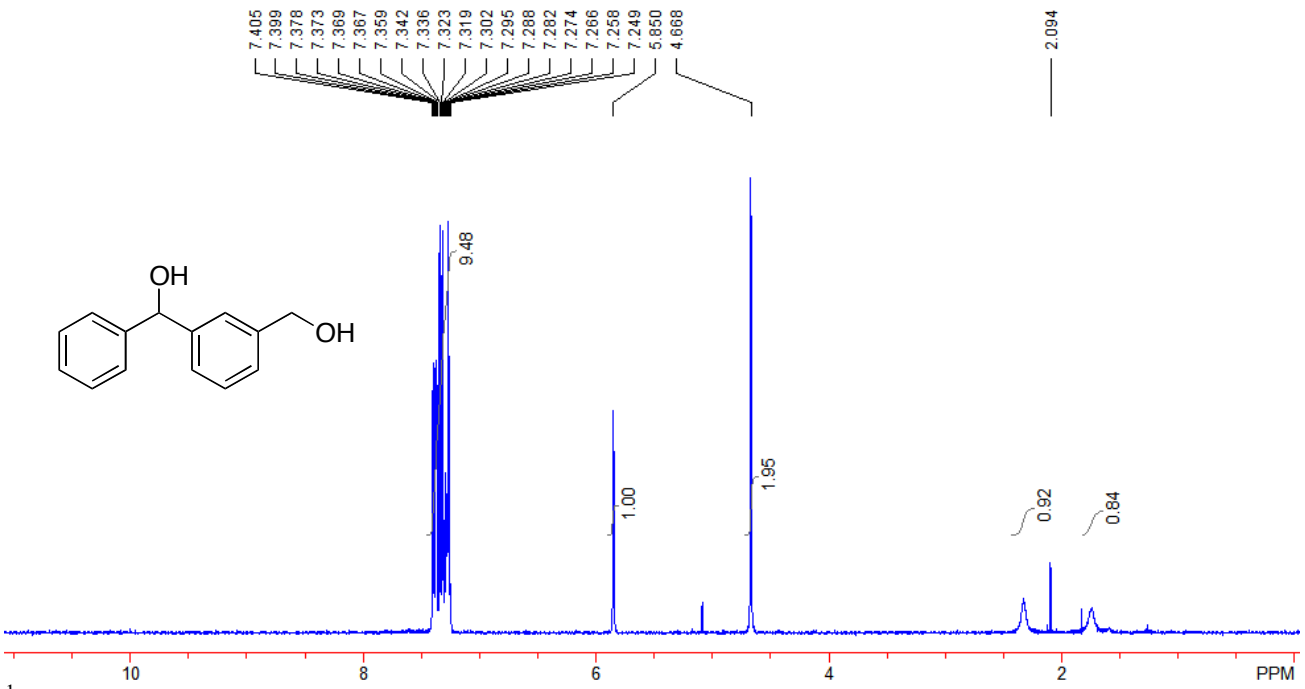
X. ^{1}H and ^{13}C NMR Spectra of Diol Substrates (1-10).



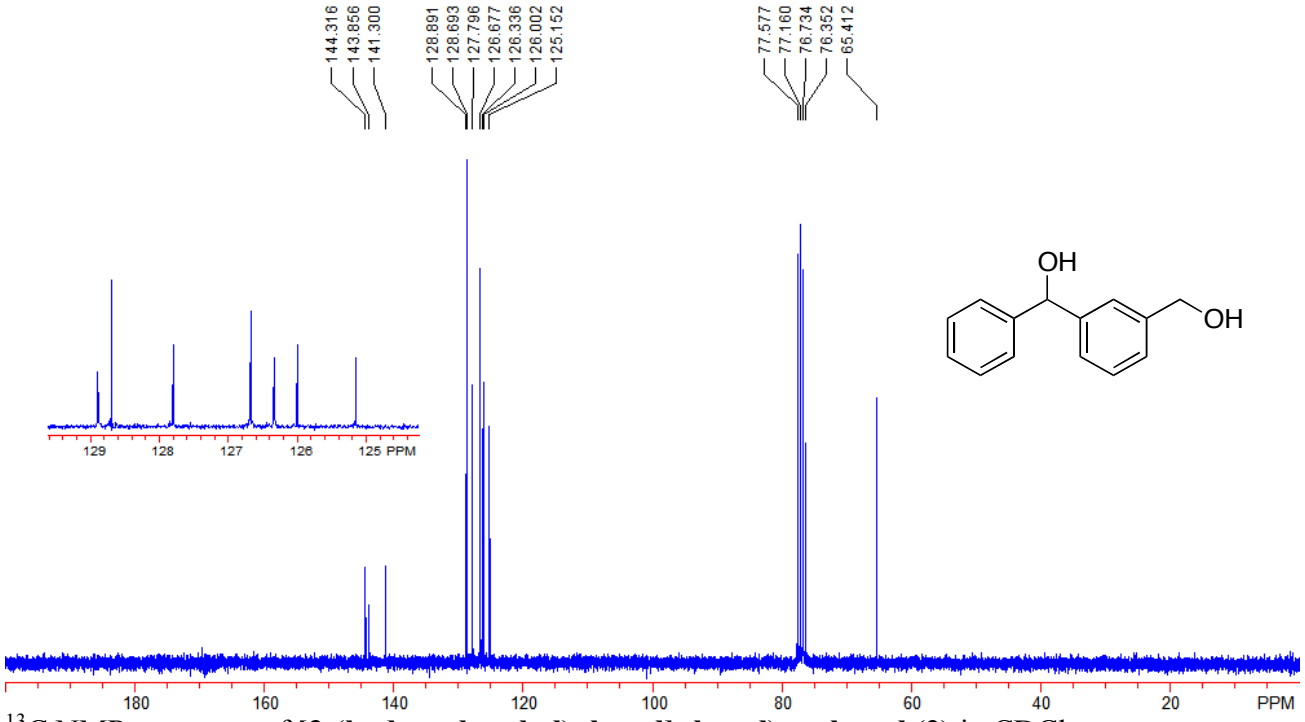
^{1}H NMR spectrum of **4-(1'-hydroxyethyl)benzyl alcohol (1)** in $CDCl_3$.



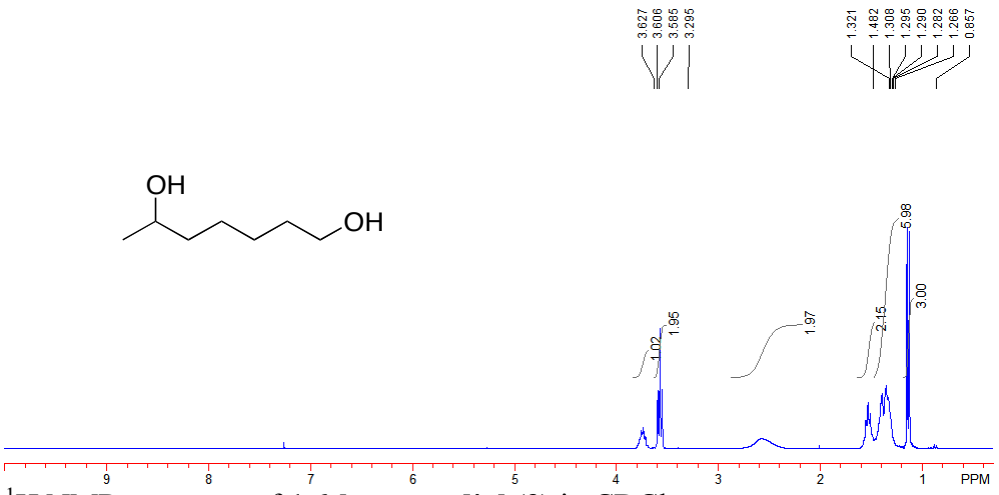
^{13}C NMR spectrum of **4-(1'-hydroxyethyl)benzyl alcohol (1)** in $CDCl_3$.



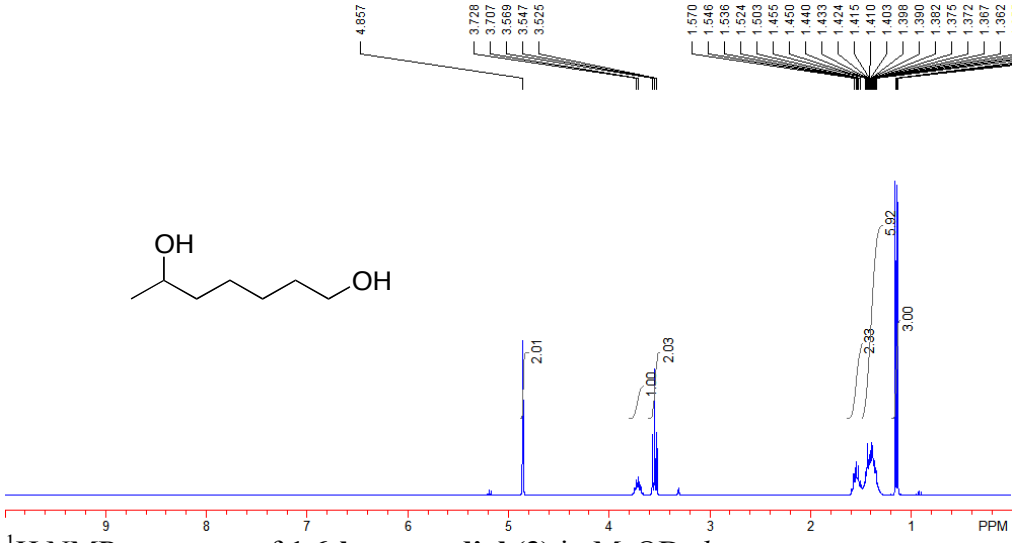
^{1}H NMR spectrum of **[3-(hydroxylmethyl)phenyl]phenyl)methanol (2)** in $CDCl_3$.



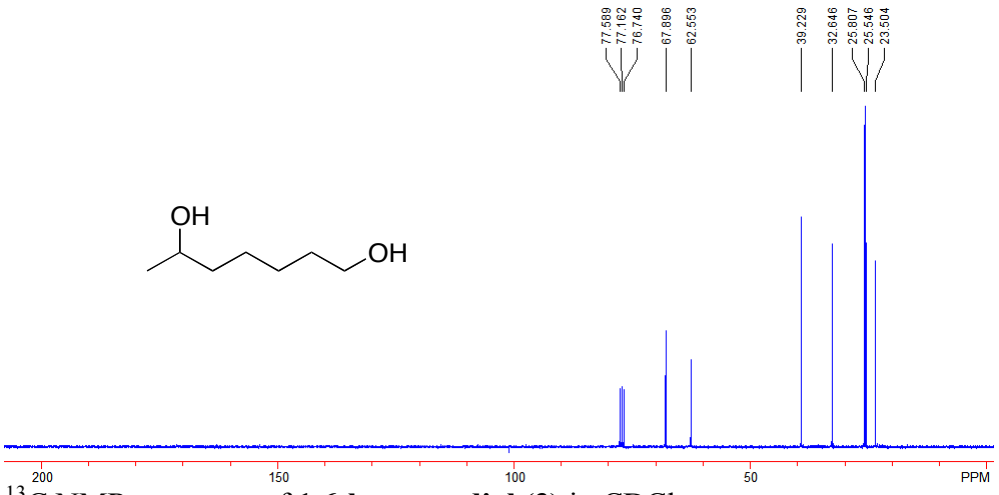
^{13}C NMR spectrum of **[3-(hydroxylmethyl)phenyl]phenyl)methanol (2)** in $CDCl_3$.



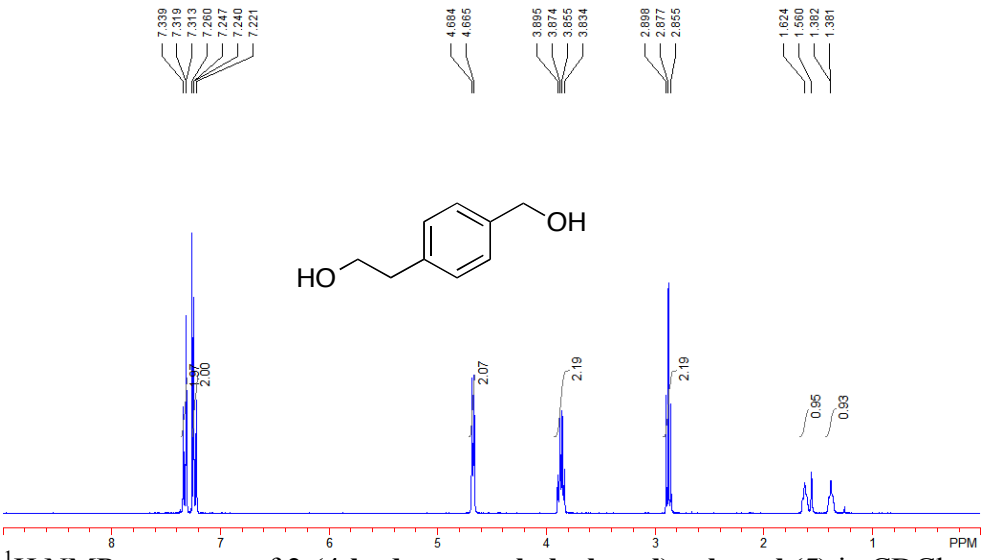
^{1}H NMR spectrum of **1,6-heptane diol (3)** in $CDCl_3$.



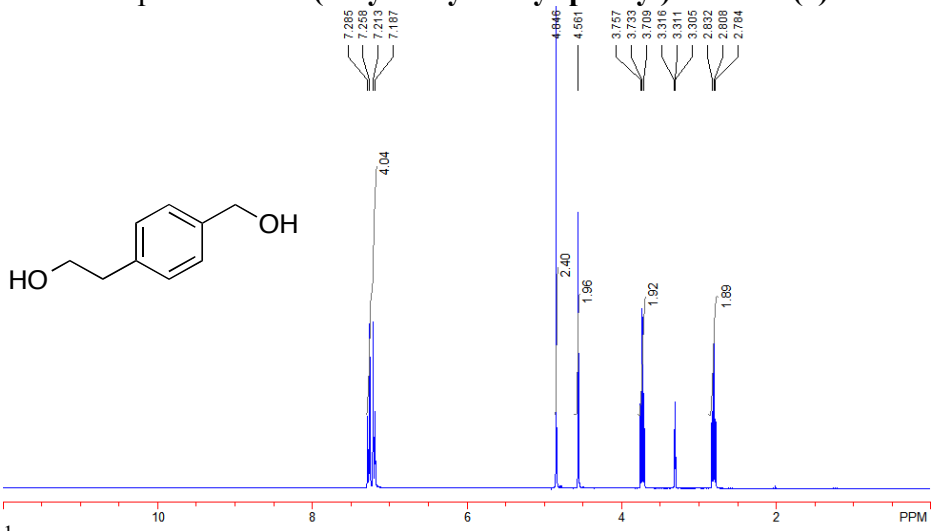
^{1}H NMR spectrum of **1,6-heptane diol (3)** in MeOD-*d*$_4$.



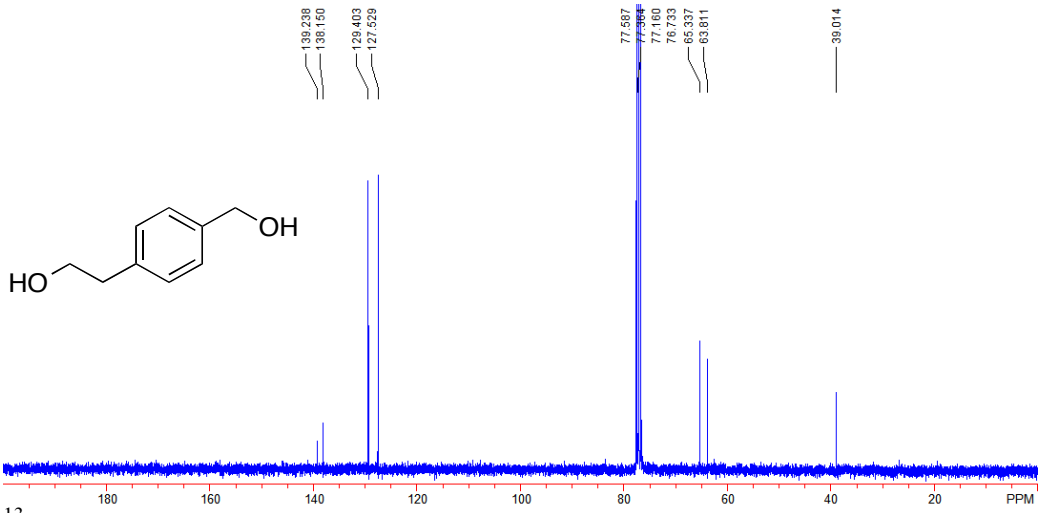
^{13}C NMR spectrum of **1,6-heptane diol (3)** in $CDCl_3$.



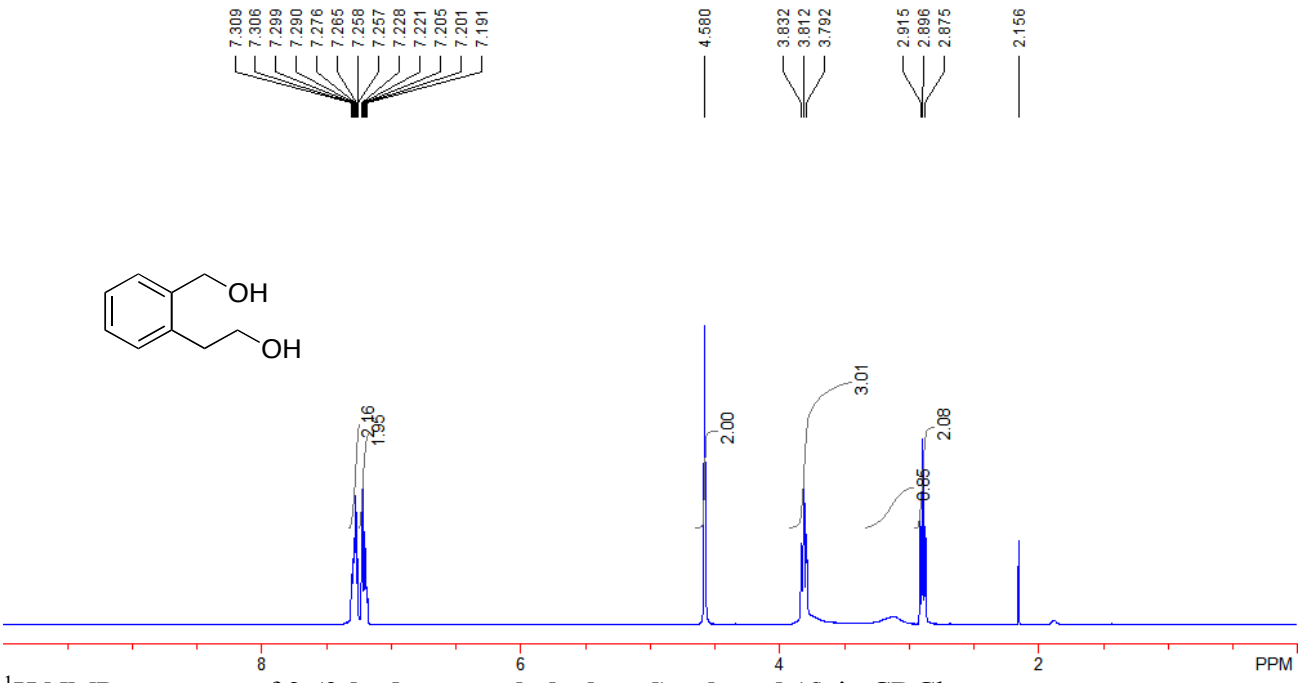
^{1}H NMR spectrum of **2-(4-hydroxymethyl-phenyl)-ethanol (5)** in $CDCl_3$.



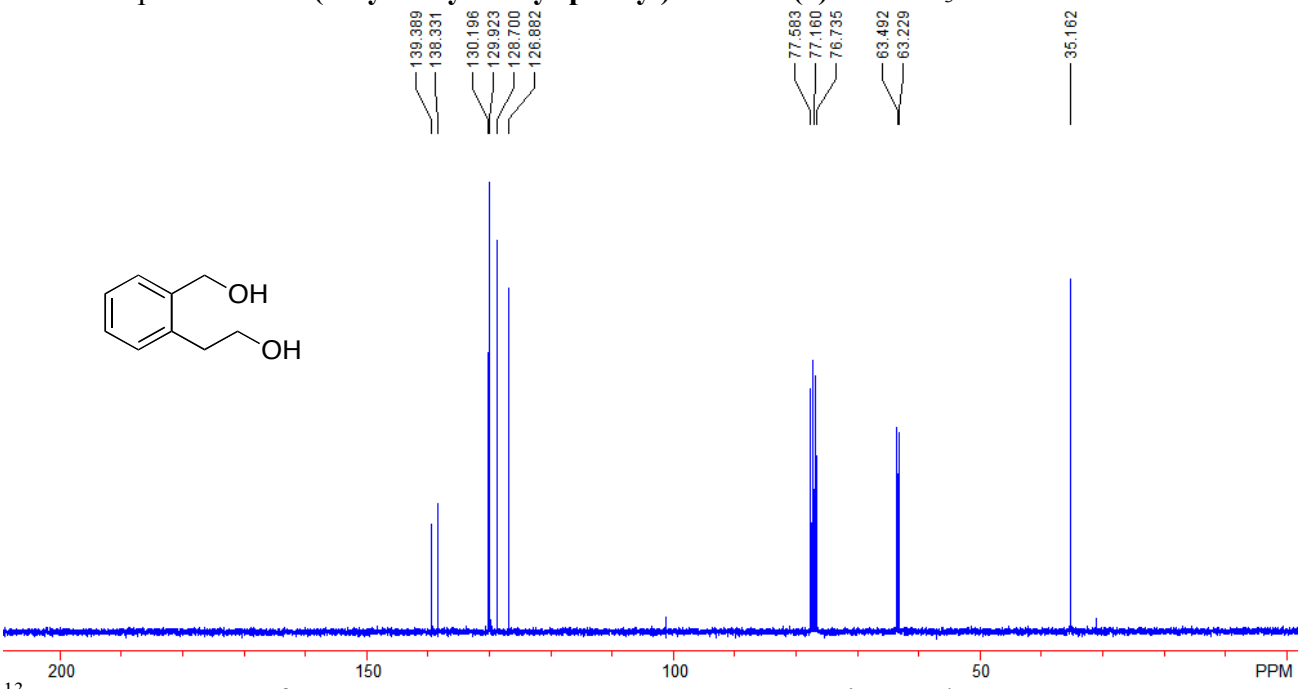
^{1}H NMR spectrum of **2-(4-hydroxymethyl-phenyl)-ethanol (5)** in MeOD-d_4.



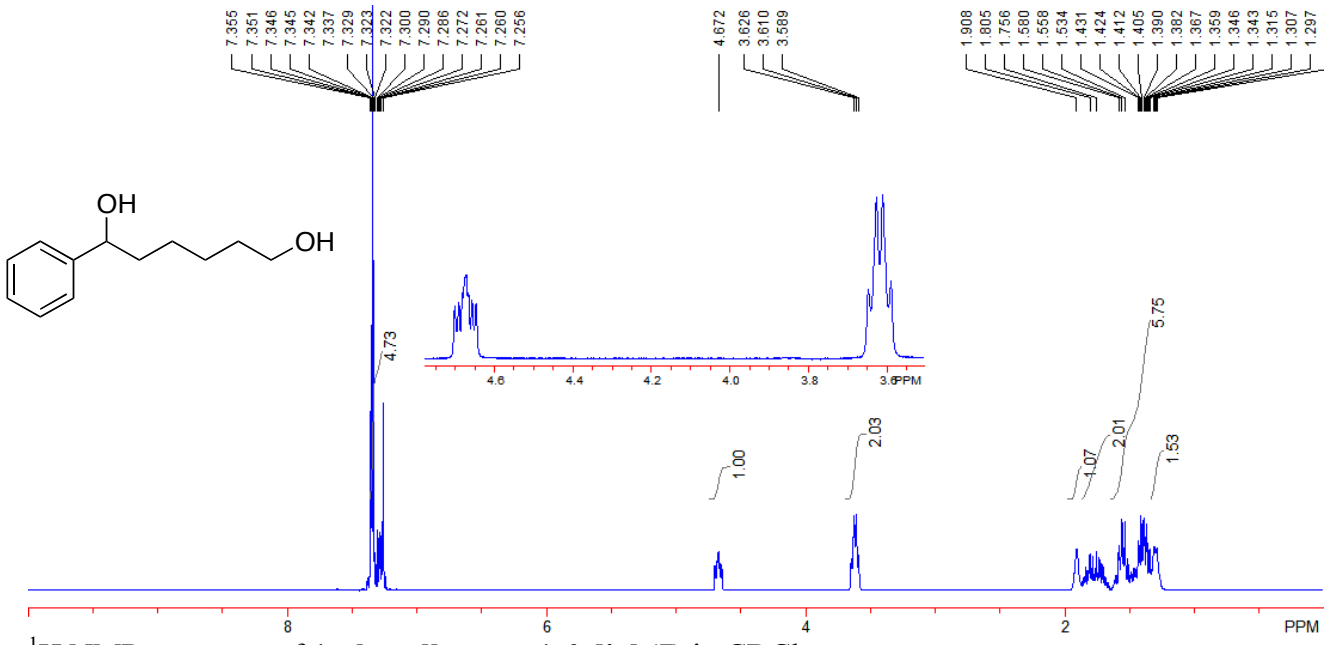
^{13}C NMR spectrum of **2-(4-hydroxymethyl-phenyl)-ethanol (5)** in $CDCl_3$.



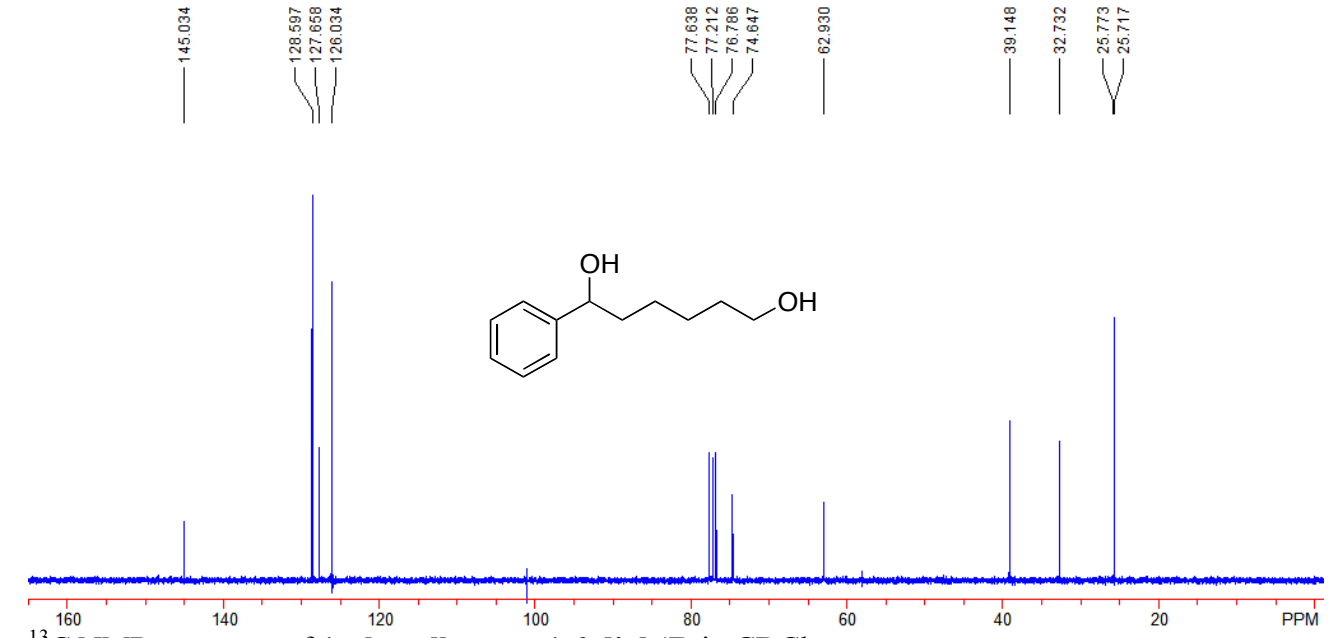
^{1}H NMR spectrum of **2-(2-hydroxymethyl-phenyl)-ethanol (6)** in $CDCl_3$.



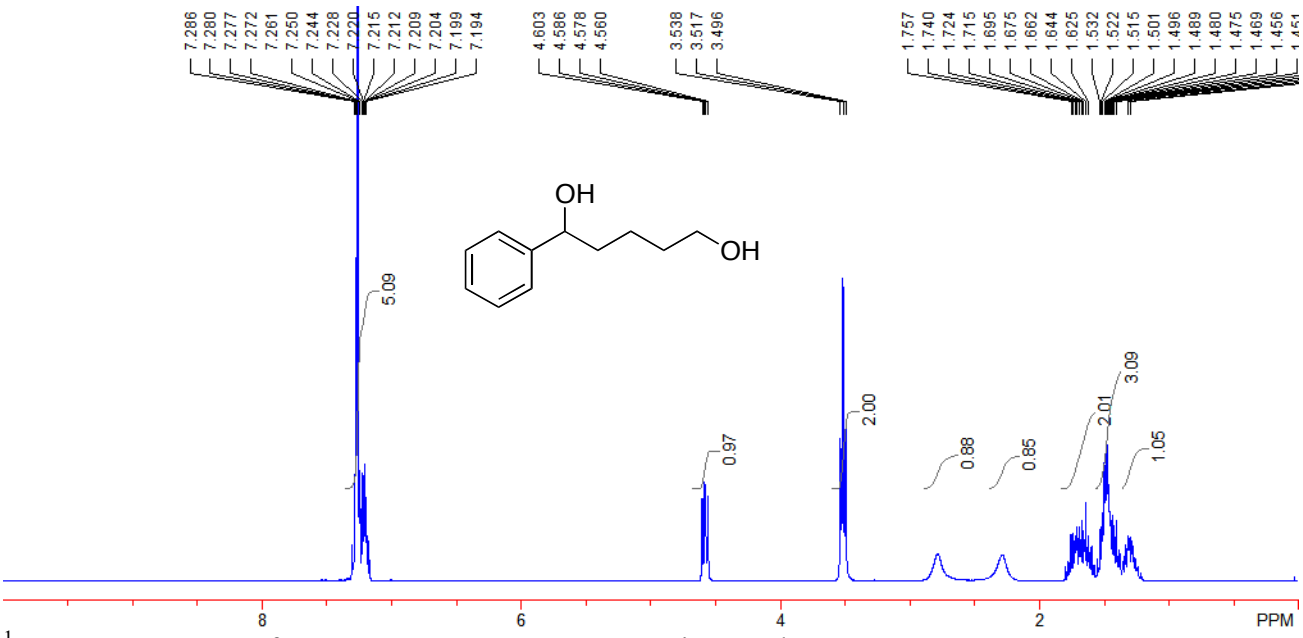
^{13}C NMR spectrum of **2-(2-hydroxymethyl-phenyl)-ethanol (6)** in $CDCl_3$.



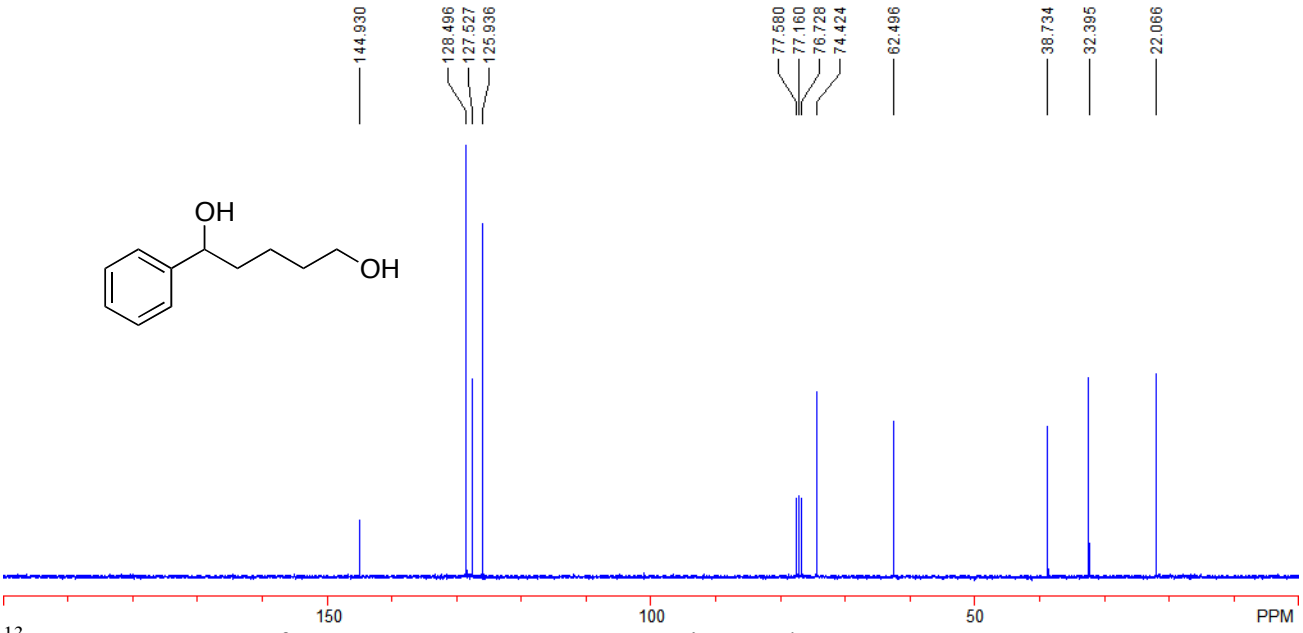
^{1}H NMR spectrum of **1-phenylhexane-1,6-diol (7)** in $CDCl_3$.



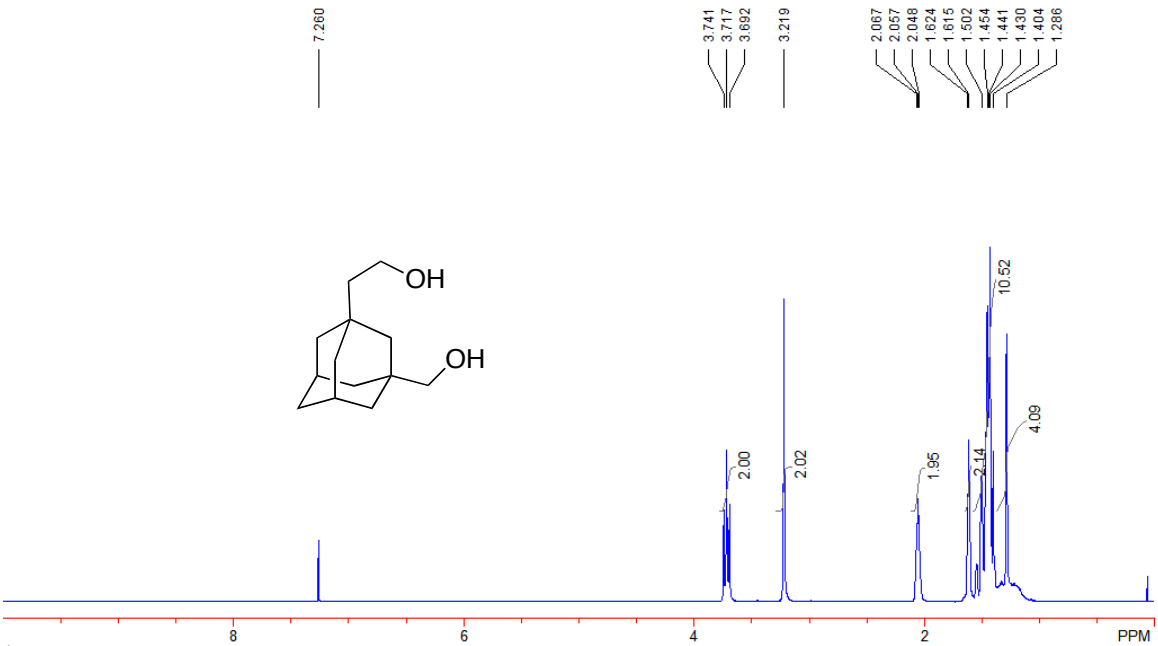
^{13}C NMR spectrum of **1-phenylhexane-1,6-diol (7)** in $CDCl_3$.



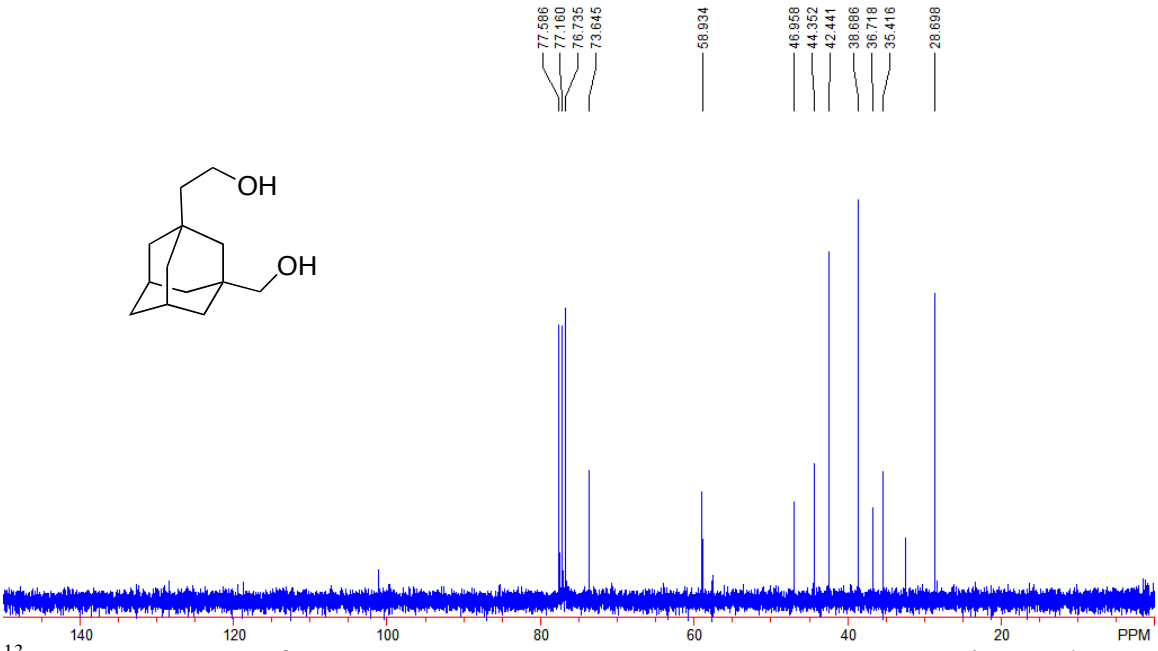
^{1}H NMR spectrum of **1-phenylpentane-1,5-diol (8)** in $CDCl_3$.



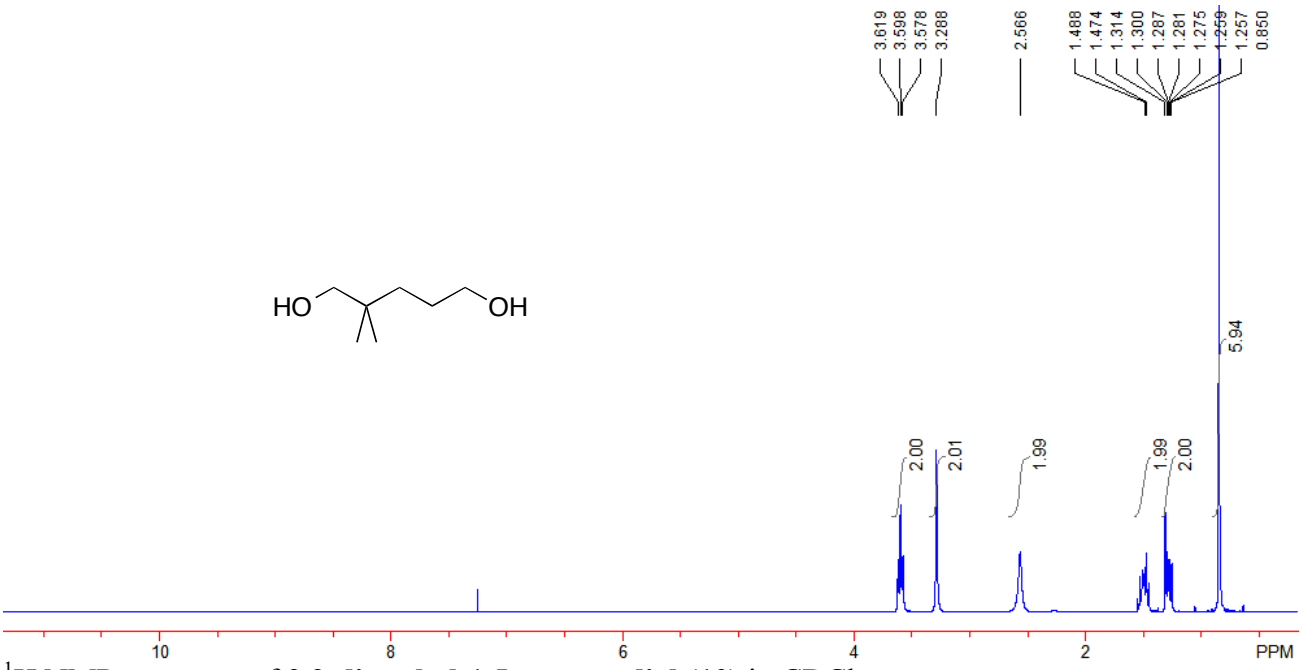
^{13}C NMR spectrum of **1-phenylpentane-1,5-diol (8)** in $CDCl_3$.



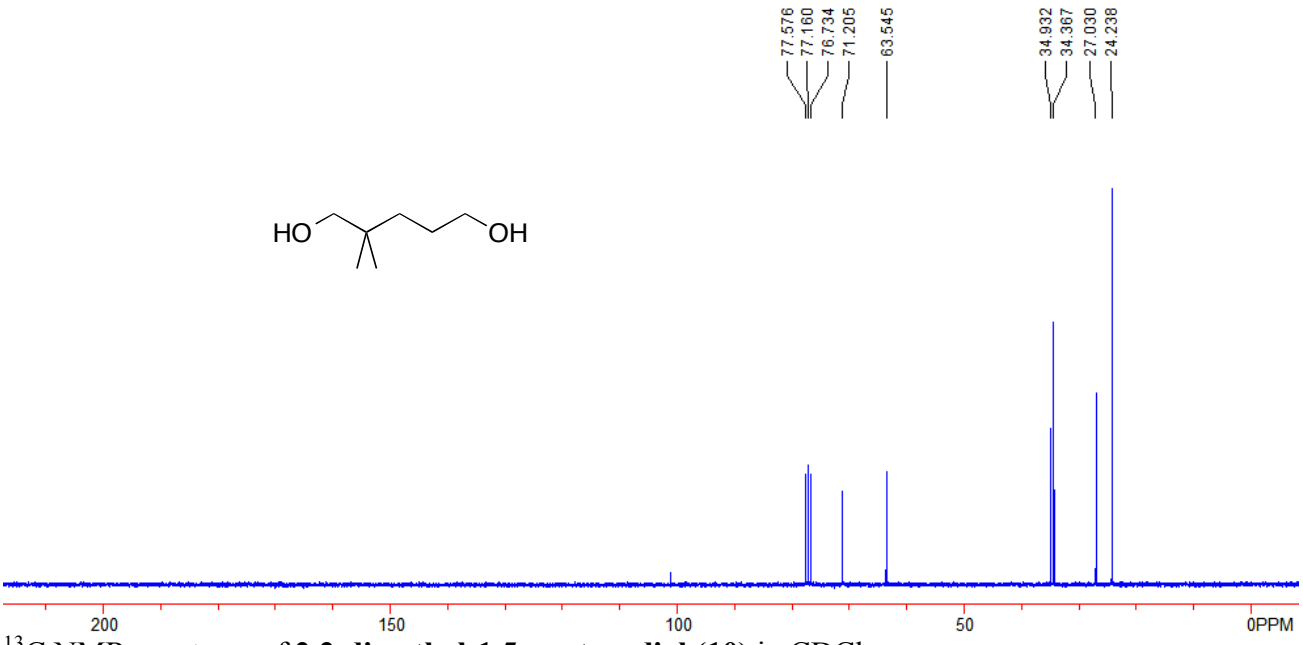
^{1}H NMR spectrum of **2-(3-hydroxymethyl-adamantan-1-yl)-ethanol (9)** in $CDCl_3$.



^{13}C NMR spectrum of **2-(3-hydroxymethyl-adamantan-1-yl)-ethanol (9)** in $CDCl_3$.

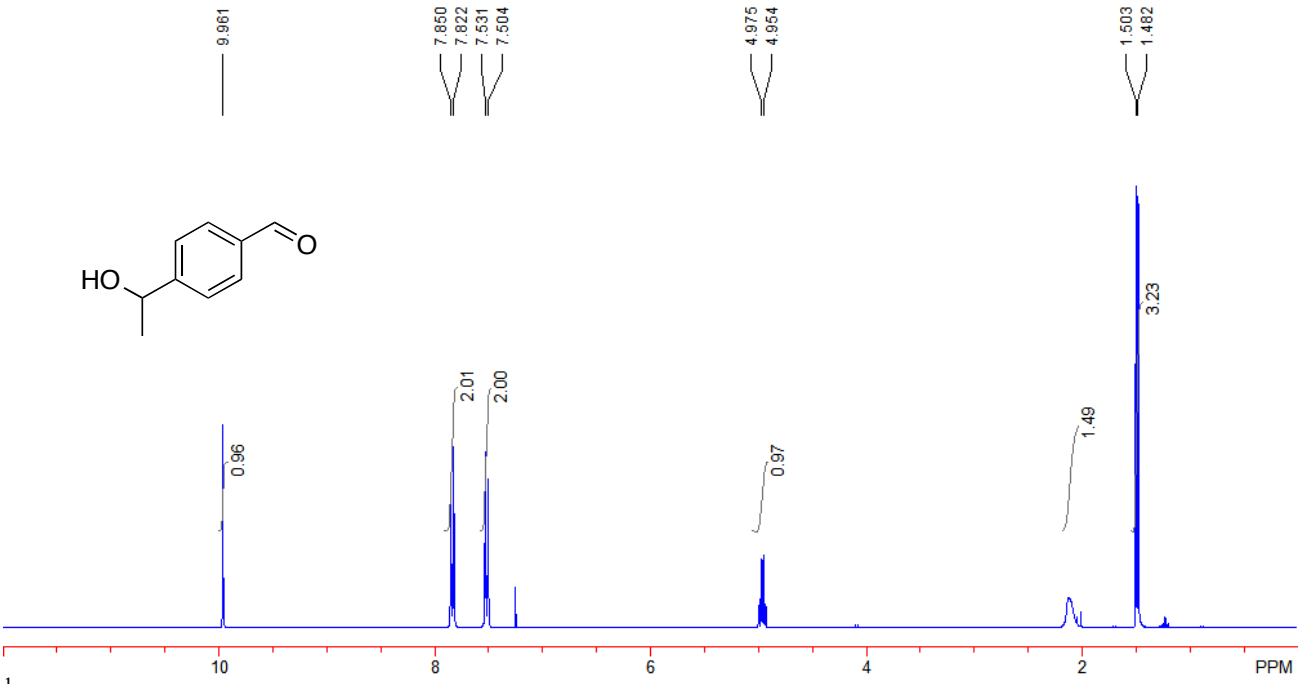


^{1}H NMR spectrum of **2,2-dimethyl-1,5-pentanediol (10)** in $CDCl_3$.

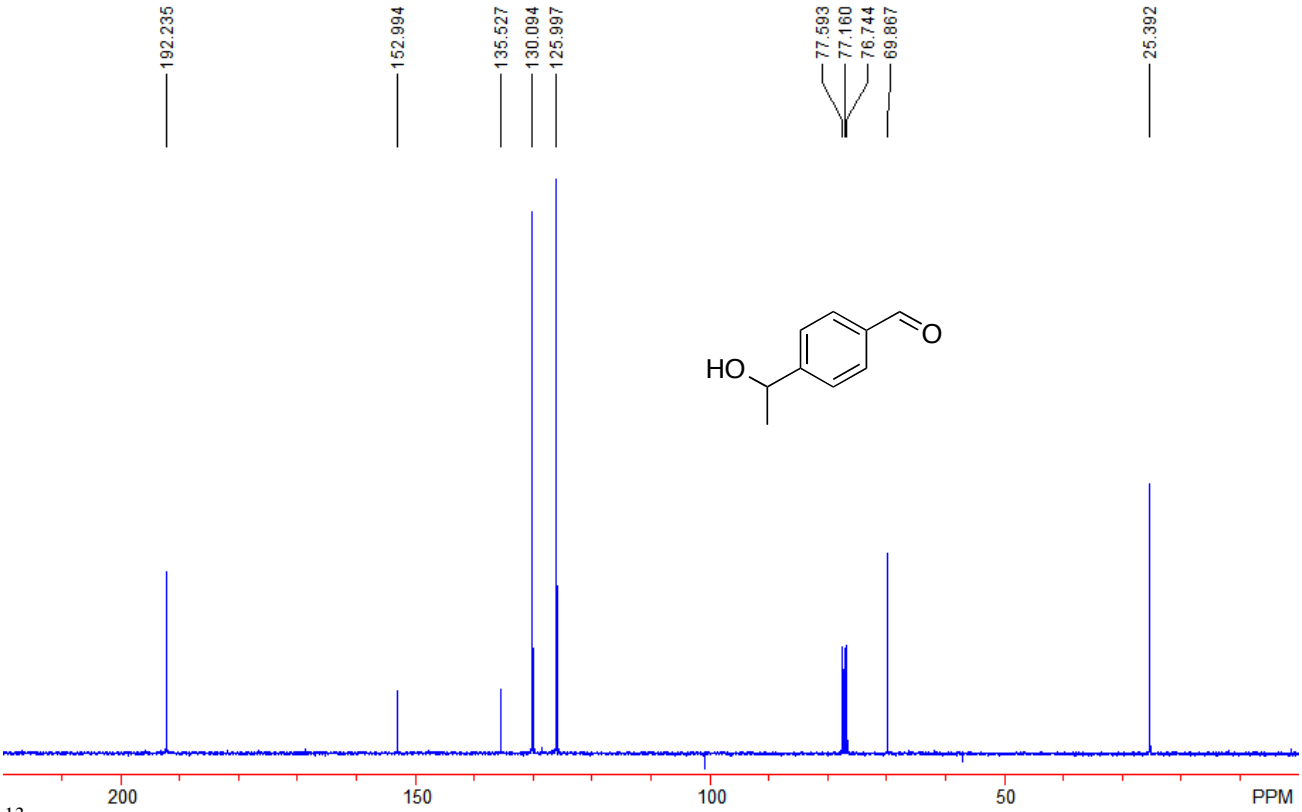


^{13}C NMR spectrum of **2,2-dimethyl-1,5-pentanediol (10)** in $CDCl_3$.

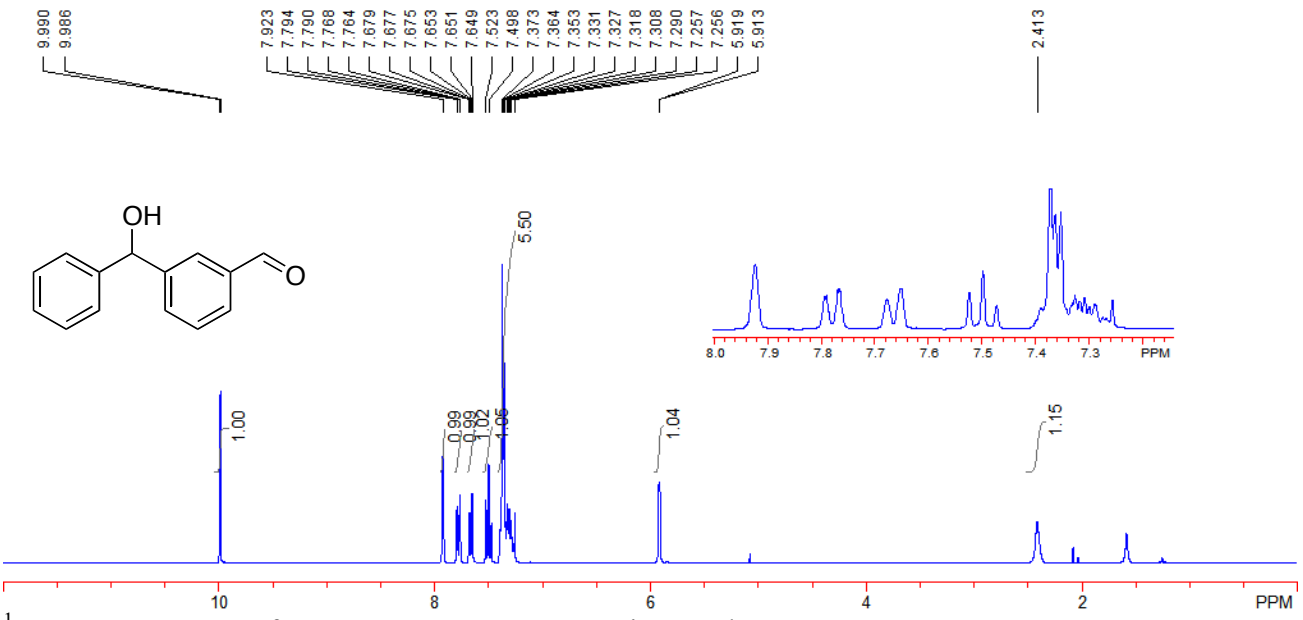
XI. ^{1}H and ^{13}C NMR Spectra of Aldehyde/Alcohol Products (11-20).



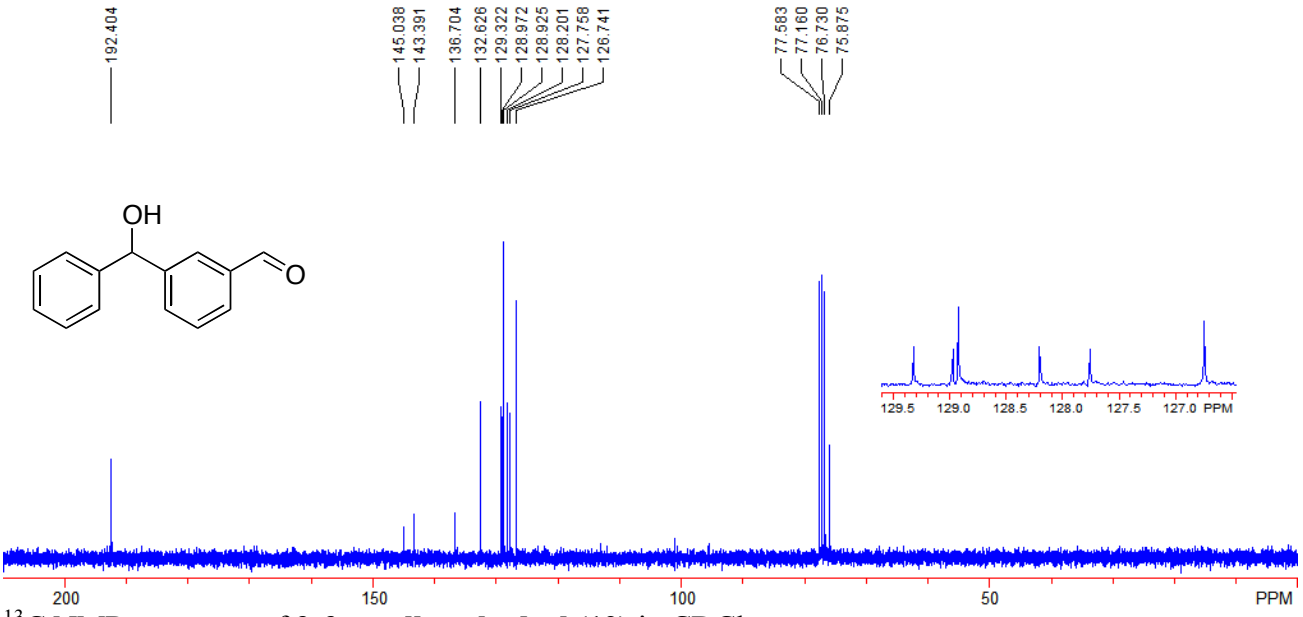
^{1}H NMR spectrum of **4-(1-hydroxyethyl)benzaldehyde (11)** in $CDCl_3$.



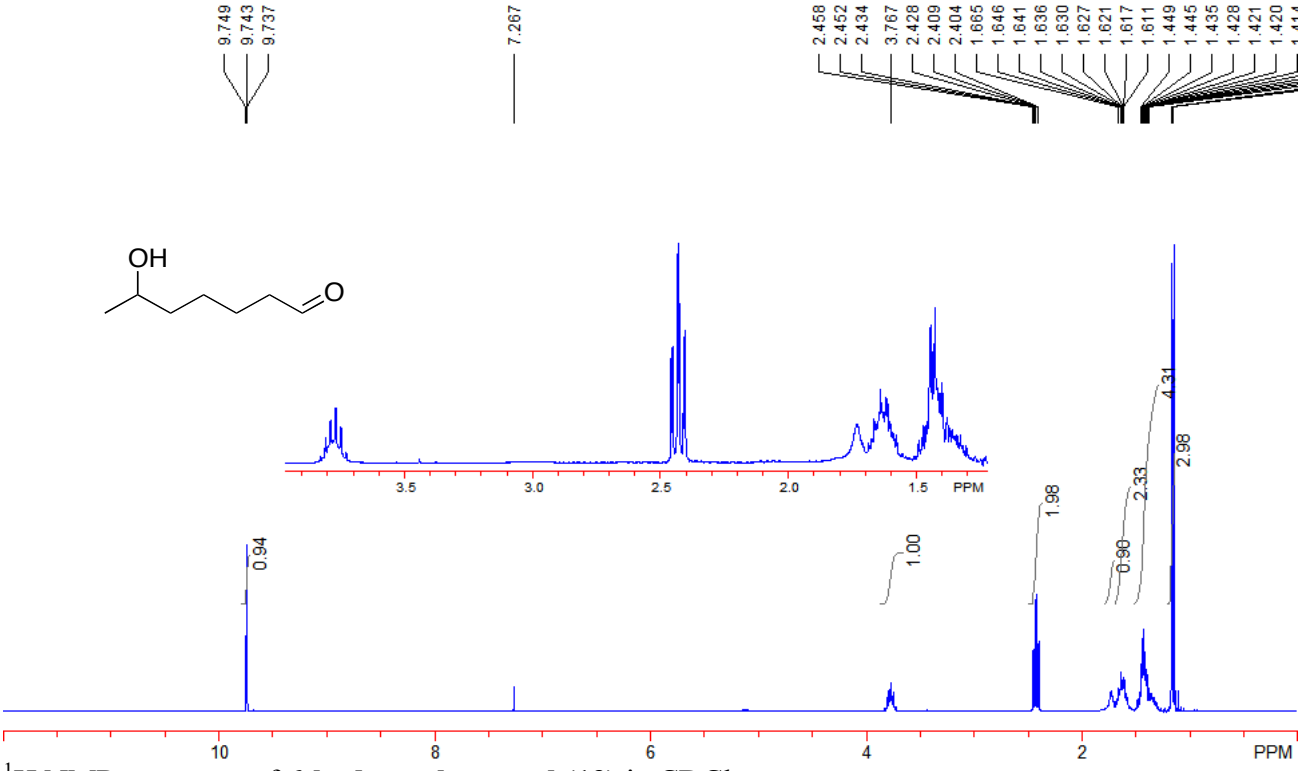
^{13}C NMR spectrum of **4-(1-hydroxyethyl)benzaldehyde (11)** in $CDCl_3$.



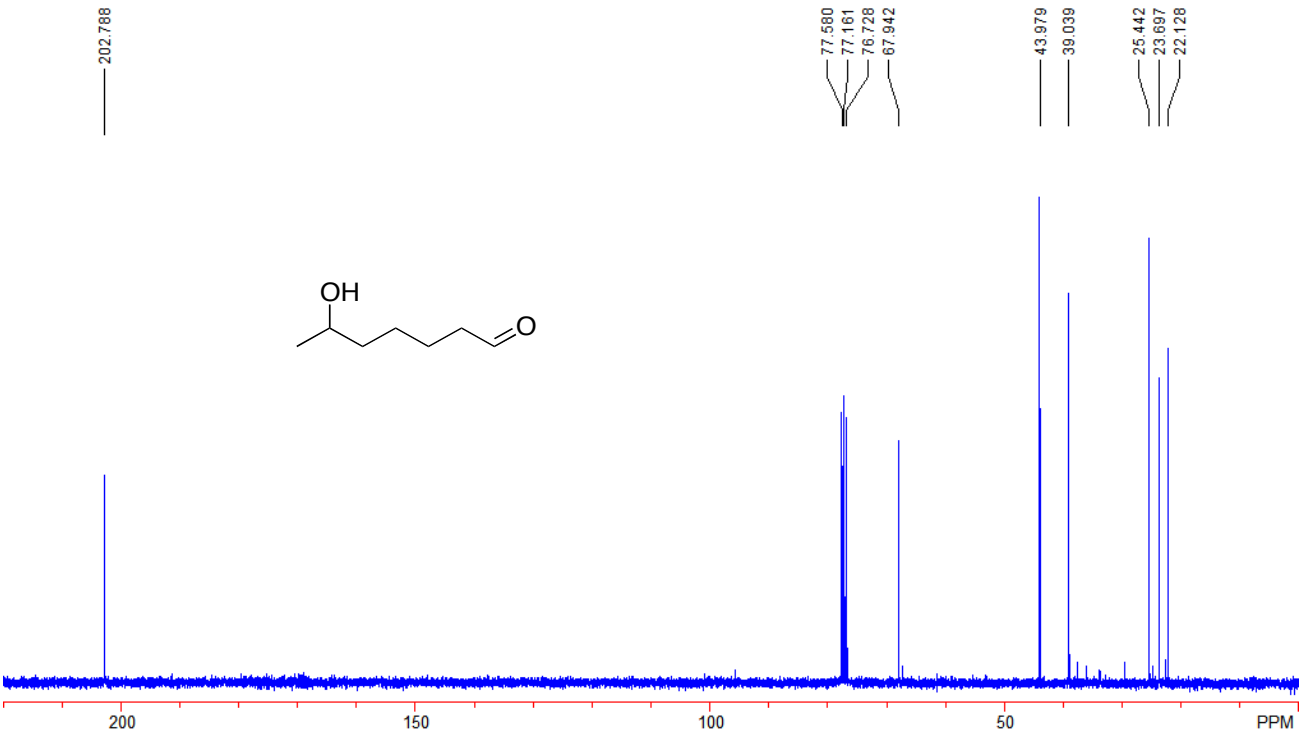
^{1}H NMR spectrum of **3-formylbenzhydrol (12)** in $CDCl_3$.



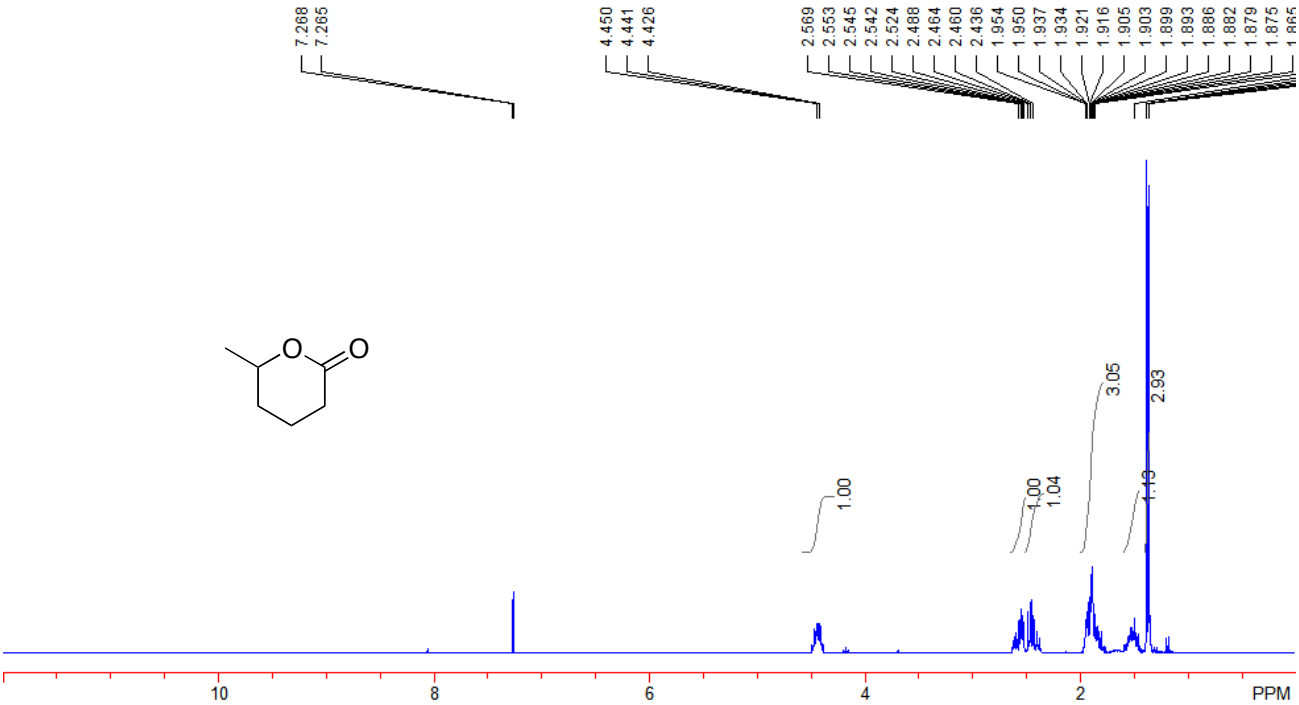
^{13}C NMR spectrum of **3-formylbenzhydrol (12)** in $CDCl_3$.



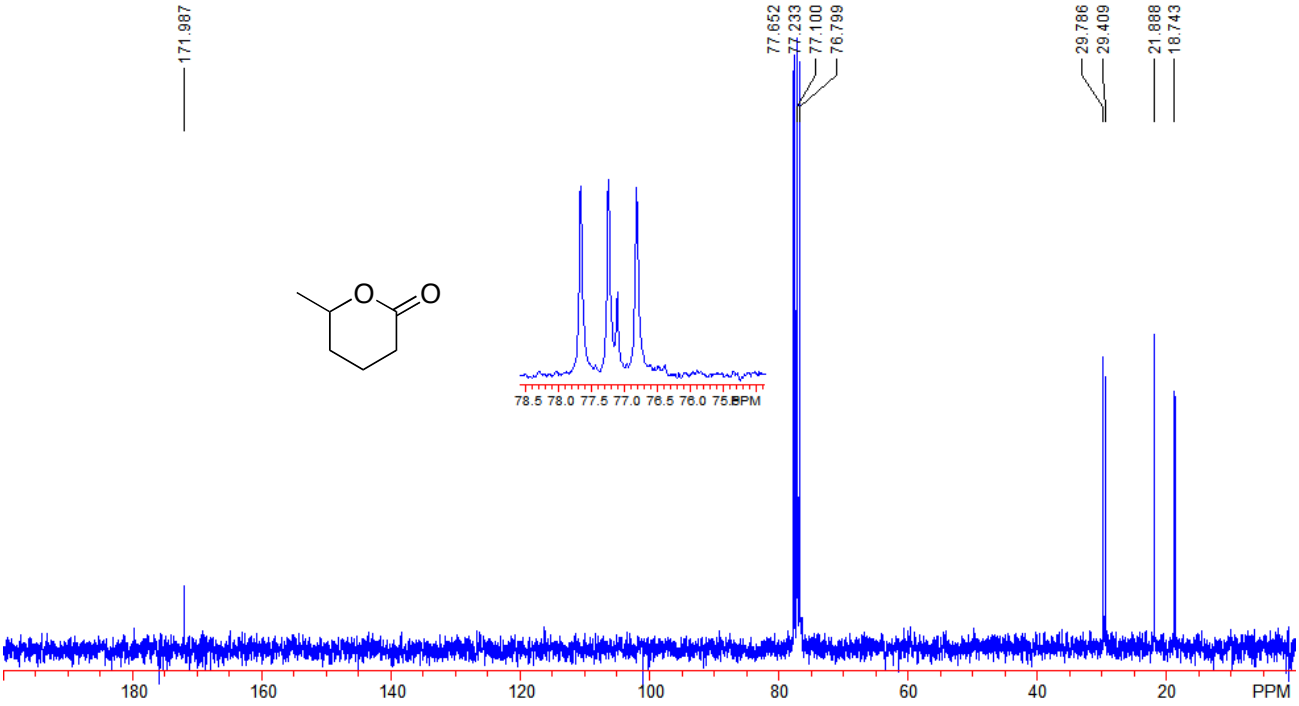
^{1}H NMR spectrum of **6-hydroxy-heptanal (13)** in $CDCl_3$.



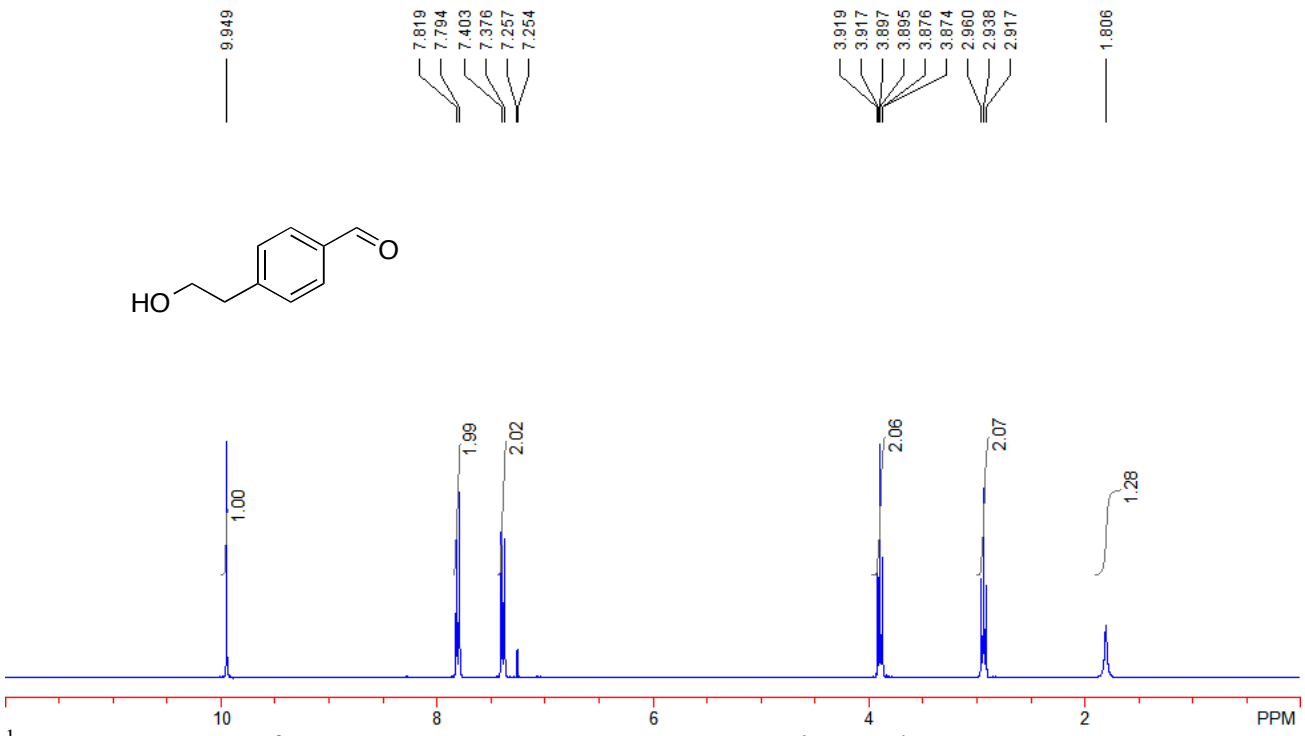
^{13}C NMR spectrum of **6-hydroxyl-heptanal (13)** in $CDCl_3$.



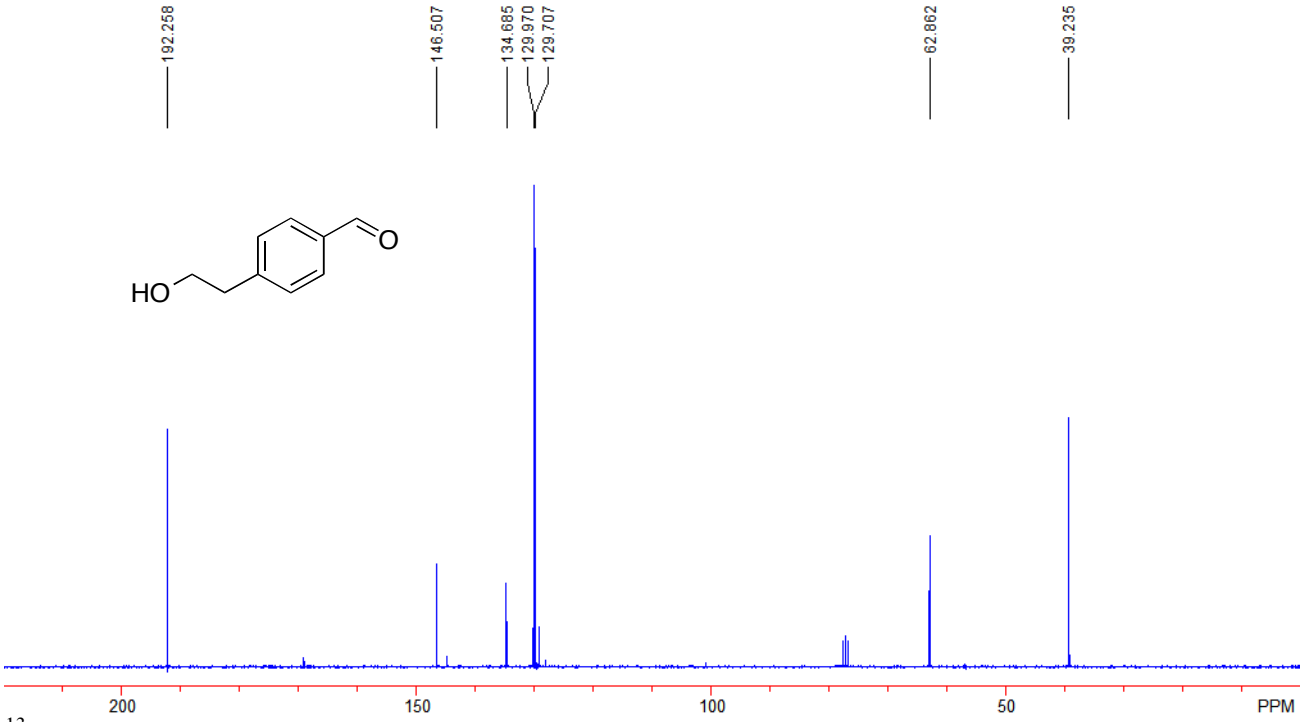
^{1}H NMR spectrum of **6-methyl-tetrahydro-pyran-2-one (14)** in $CDCl_3$.



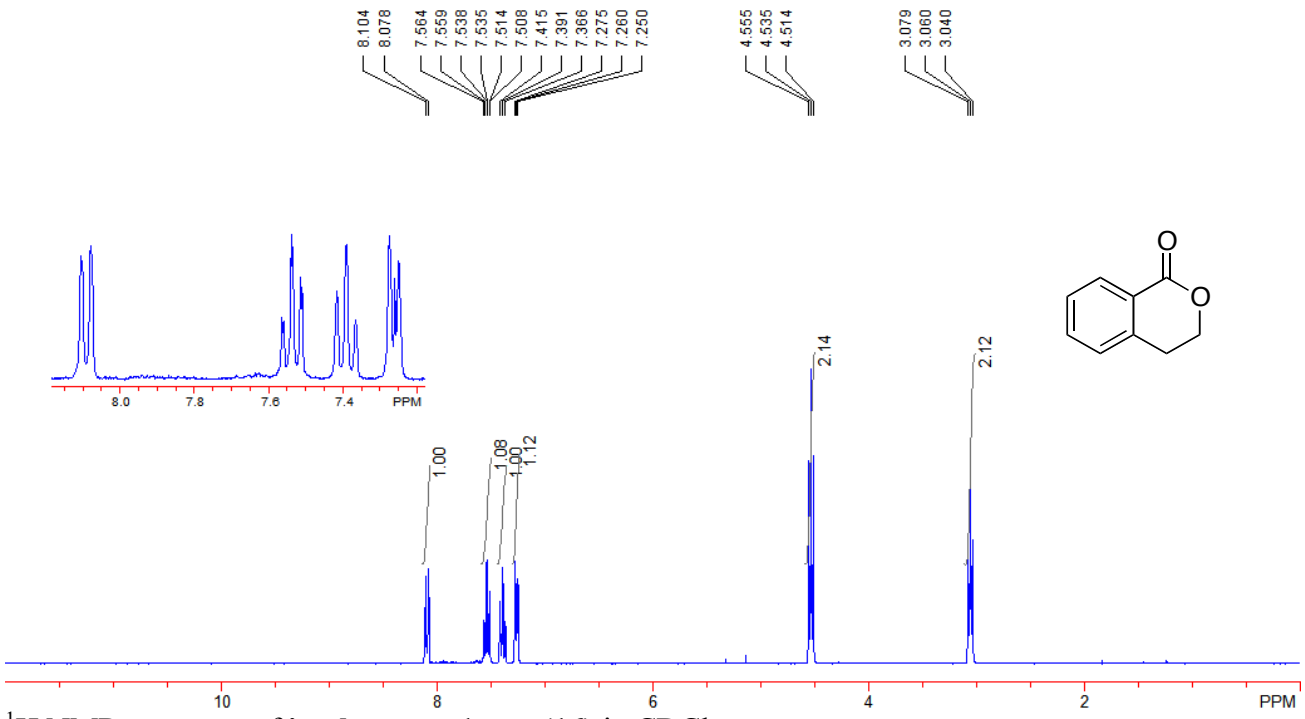
^{13}C NMR spectrum of **6-methyl-tetrahydro-pyran-2-one (14)** in $CDCl_3$.



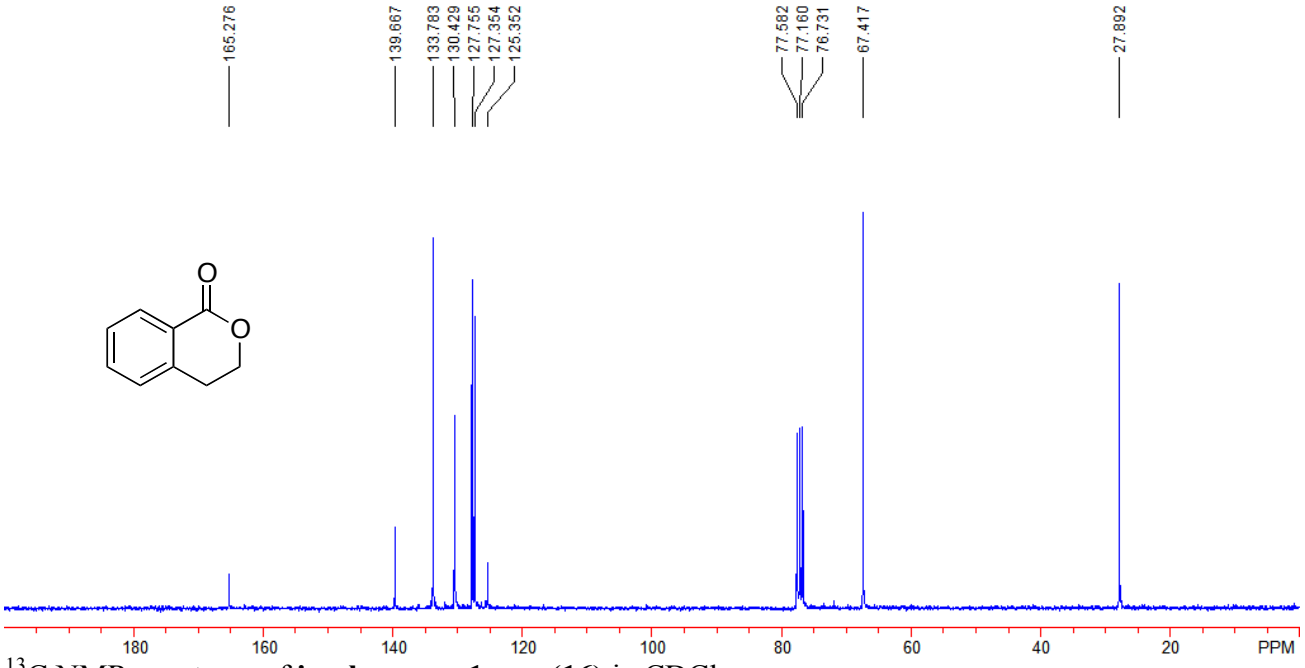
^{1}H NMR spectrum of **4-(2-hydroxyethyl)benzaldehyde (15)** in $CDCl_3$.



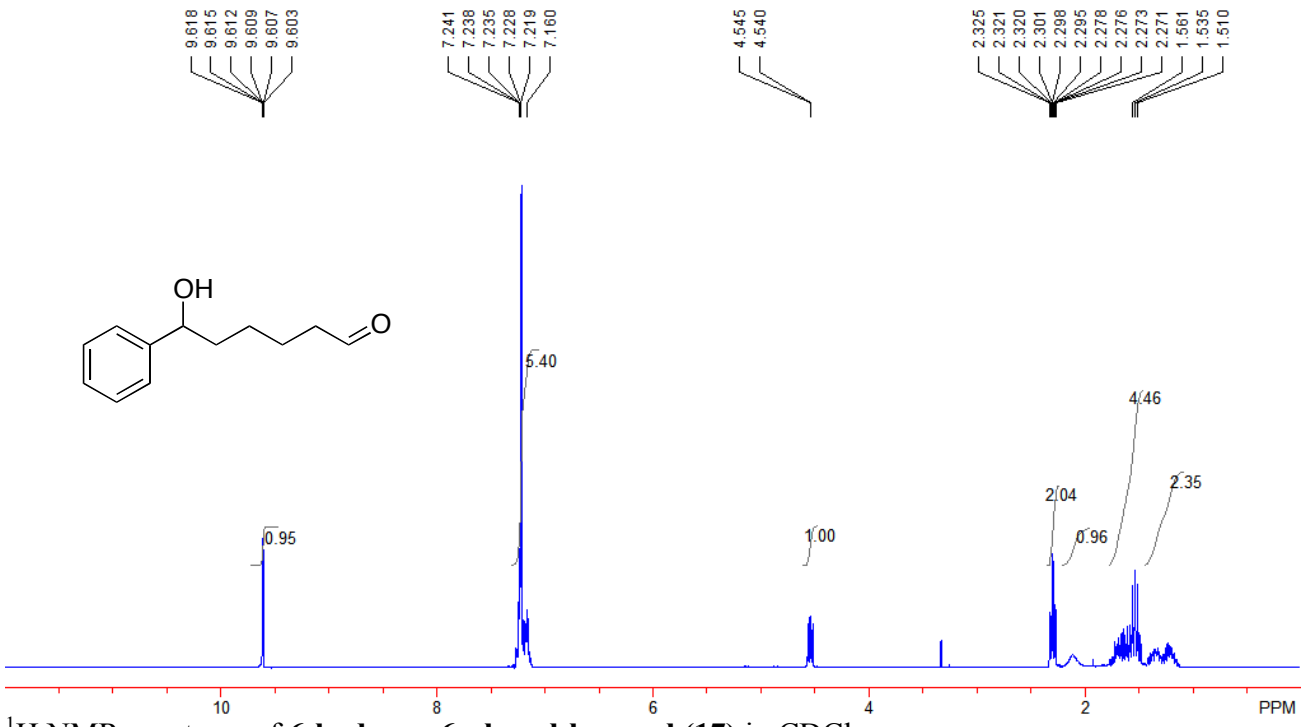
^{13}C NMR spectrum of **4-(2-hydroxyethyl)benzaldehyde (15)** in $CDCl_3$.



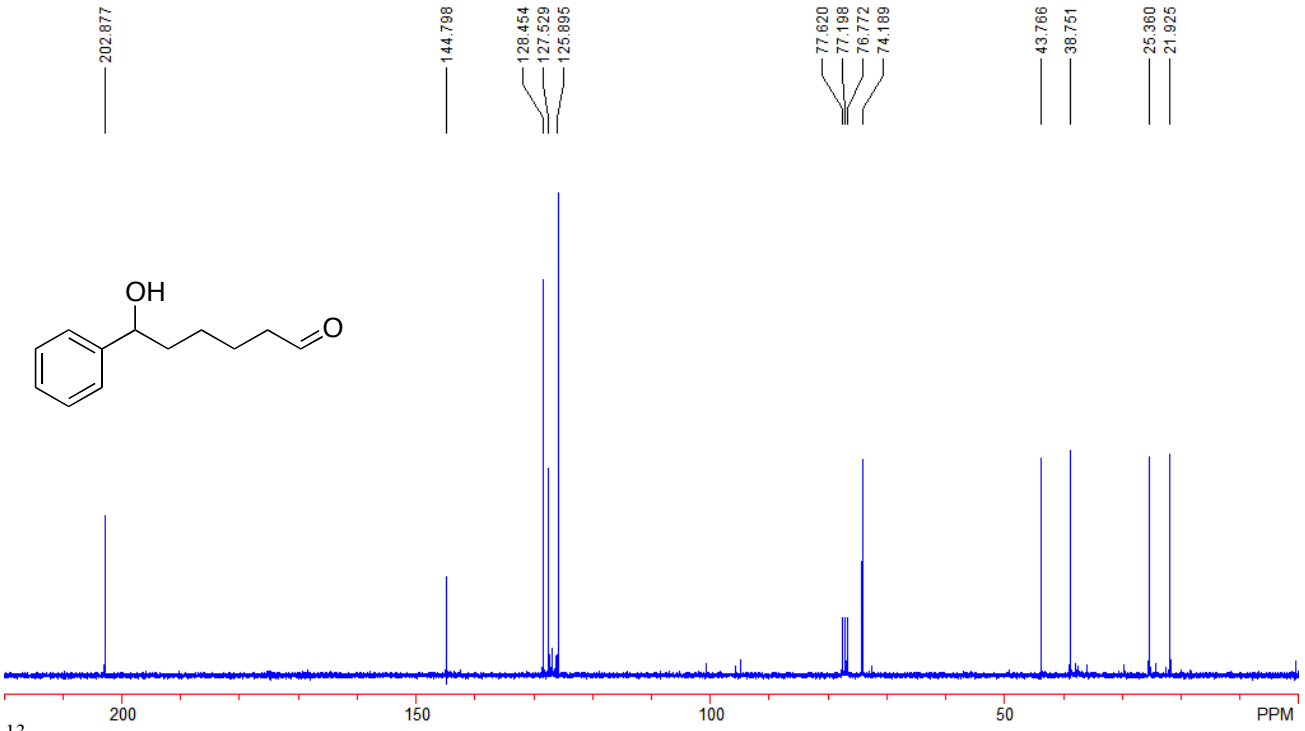
^{1}H NMR spectrum of **isochroman-1-one (16)** in $CDCl_3$.



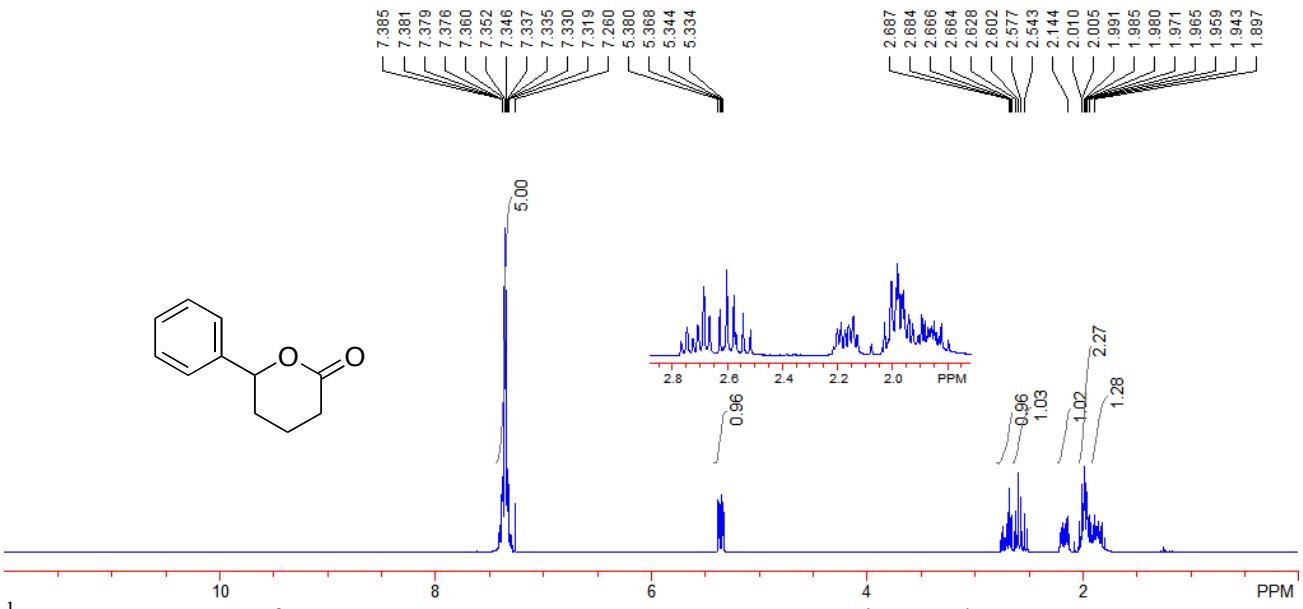
^{13}C NMR spectrum of **isochroman-1-one (16)** in $CDCl_3$.



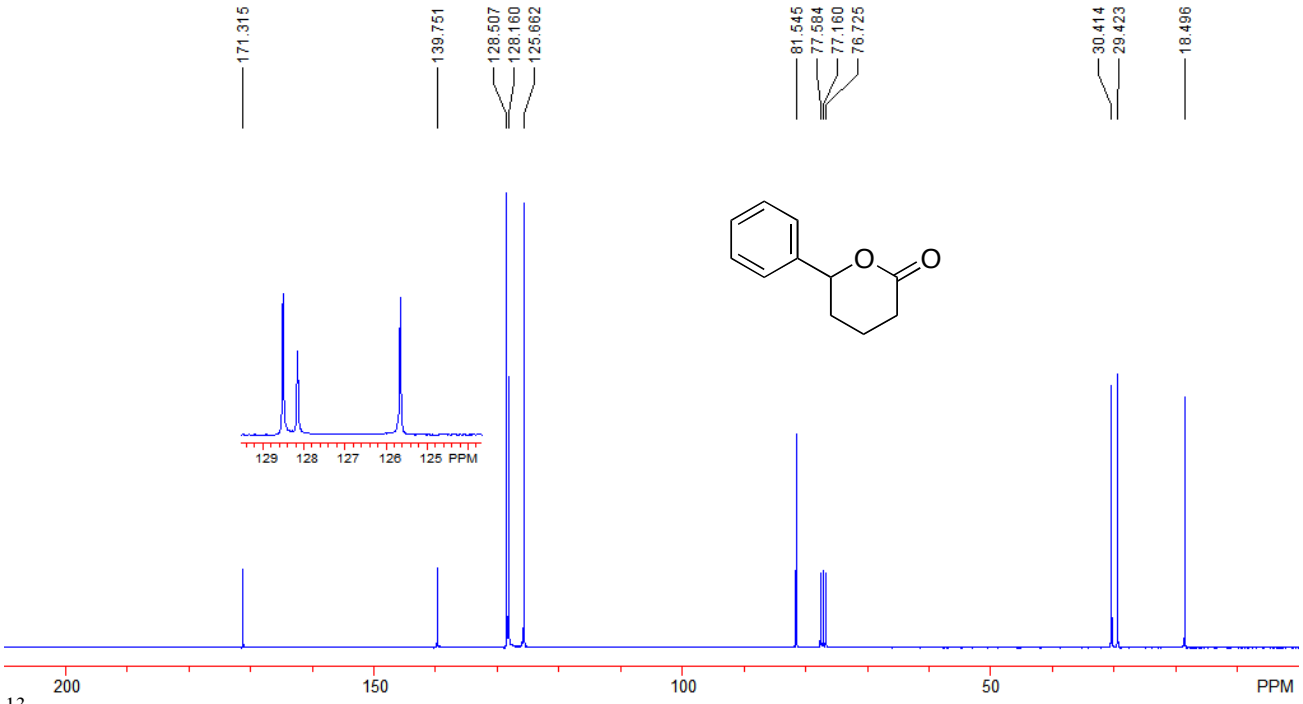
^{1}H NMR spectrum of **6-hydroxy-6-phenyl-hexanal (17)** in $CDCl_3$.



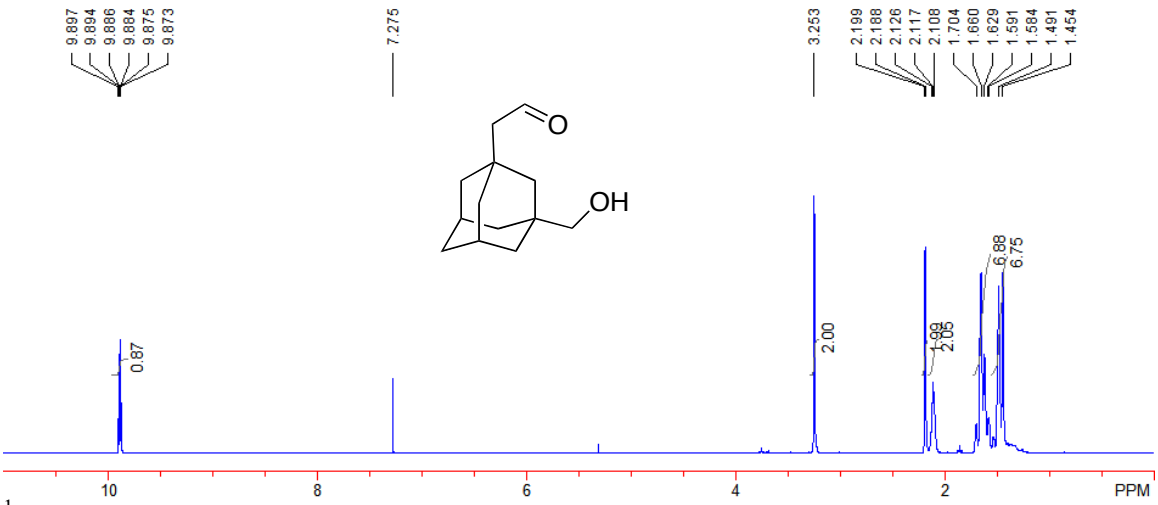
^{13}C NMR spectrum of **6-hydroxy-6-phenyl-hexanal (17)** in $CDCl_3$.



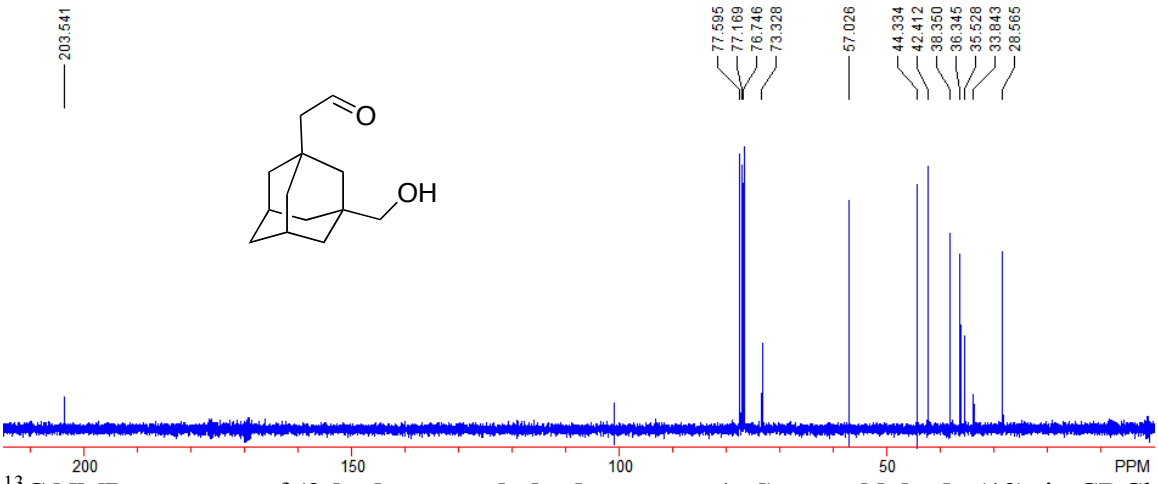
^{1}H NMR spectrum of **6-phenyl-tetrahydro-2*H*-pyran-2-one (18)** in $CDCl_3$.



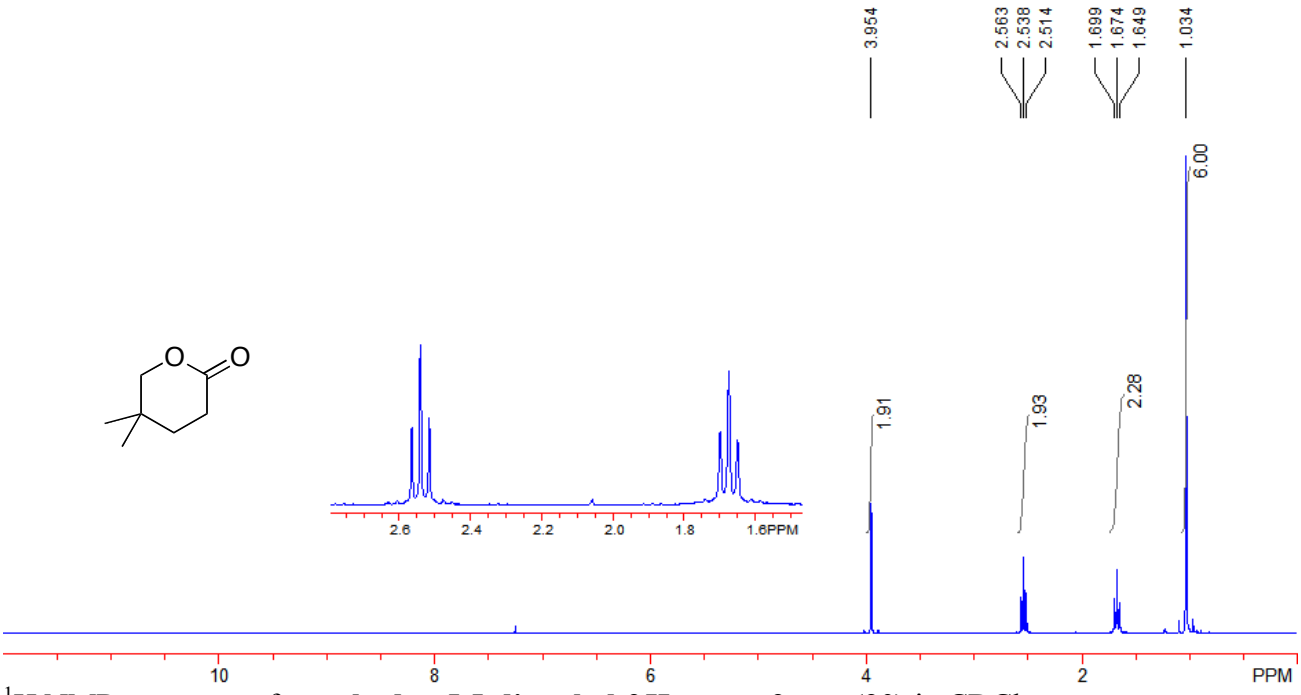
^{13}C NMR spectrum of **6-phenyl-tetrahydro-2*H*-pyran-2-one (18)** in $CDCl_3$.



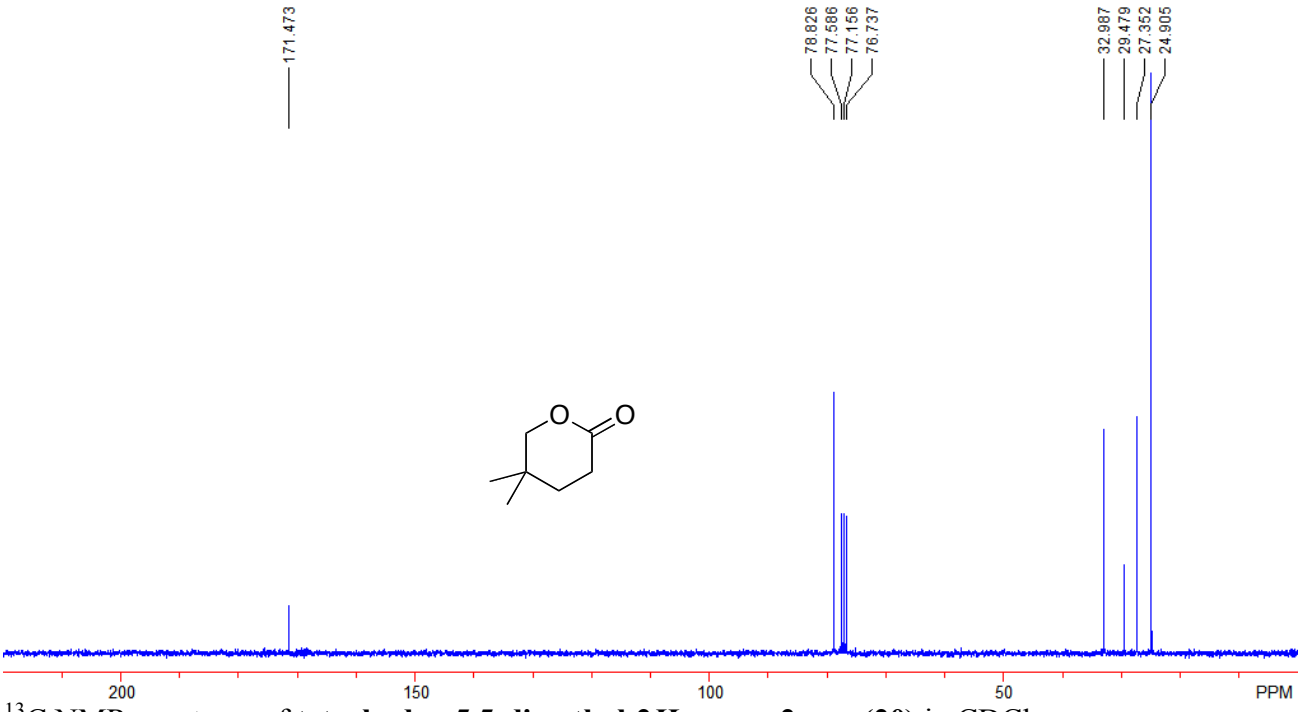
^{1}H NMR spectrum of **(3-hydroxymethyl-adamantan-1-yl)-acetaldehyde (19)** in $CDCl_3$.



^{13}C NMR spectrum of **(3-hydroxymethyl-adamantan-1-yl)-acetaldehyde (19)** in $CDCl_3$.



^{1}H NMR spectrum of **tetrahydro-5,5-dimethyl-2*H*-pyran-2-one (20)** in $CDCl_3$.



^{13}C NMR spectrum of **tetrahydro-5,5-dimethyl-2*H*-pyran-2-one (20)** in $CDCl_3$.